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Original Research

Impact of Emissions on Atmospheric Composition at Kasprowy Wierch Based on Results of Carbon Monoxide and Carbon Dioxide Monitoring

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Abstract

The high-altitude laboratory of greenhouse gas measurement, KASLAB, was founded on the Polish mountain Kasprowy Wierch in 1994. In the direct neighborhood of the measuring point there are no significant sources of compounds measured at the station. However, the measuring point may be affected by periodic anthropogenic emissions from the nearby Podhale region, with Zakopane the most popular tourist resort (6 km to the north and 1 km below Kasprowy Wierch). Periodic air enrichment in CO content detected at the KASLAB station indicates a prior contact of air masses that reach Kasprowy Wierch with the lower layer of the troposphere and can be used for qualitative and quantitative evaluation of trace gas emissions (for example CO_2) from regions with strong anthropopression. Data analysis performed for 2010 presented in this paper revealed that the anthropogenic component of carbon dioxide observed at Kasprowy Wierch usually does not exceed 2 ppm, occasionally reaching a value of 10 ppm. Respiration component of atmospheric CO_2 concentration at Kasprowy Wierch can be as high as 35 ppm.

Keywords: carbon monoxide, carbon dioxide, anthropogenic emissions

Introduction

Observations of the carbon cycle are extremely important according to the political and economic consequences of climate change [1]. Carbon dioxide concentration is monitored using the great network systems like NOAA as well as single stations and then linked to the flux distribution by modeling of atmospheric processes. Estimation of anthropogenic influence on CO_2 concentration levels is currently the primary goal of many international science projects. In Europe, even remote sites stay under the influence of anthropogenic emissions as more than 30% of continental carbon dioxide has such origination [2, 3]. The anthropogenic fraction may be experimentally determined using different tracer techniques [4, 5].

Continuous measurements of CO_2 in Poland are regularly conducted only at Kasprowy Wierch [6-8]. However, $^{14}CO_2$, which is the best tracer, also is analyzed at the station but only monthly integrated values are available [9]. More frequent high precision radiocarbon sampling is very expensive and carbon monoxide may take over the role of high frequency tracers for anthropogenic fractions of carbon dioxide [10, 11]. The main sources of carbon monoxide are different combustion processes. Their origin may be natural, but more frequently are managed by human activity (anthropogenic). Carbon monoxide average lifetime in

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the atmosphere is relatively short (a few months at medium latitudes [12]). The basic process leading to CO removal from the atmosphere is the reaction with OH* radicals [13]. The concentration of CO in urban air of Polish agglomerations very often reaches a value close to the upper limit of quality standard (for Zakopane it is a 4 ppm [14]). While the background value of CO mixing ratio for latitude of Kasprowy Wierch as calculated by Globalview does not exceed 150 ppb [15], carbon monoxide concentration levels observed in the center of Zakopane often are higher than 2 ppm. This is a result of significant emissions of this gas from the city area and the specific position of Zakopane within the Podhale Trench. Relatively frequent temperature inversions and poor ventilation observed inside this trench can support accumulation of gases from the so-called low emission in the lower troposphere (CO_2, CO, SO_x, NO_x). Carbon dioxide belongs to a group of greenhouse gases and its concentration has been measured regularly at Kasprowy Wierch since the mid 90s [16].

The carbon monoxide concentration measurements at Kasprowy Wierch, started in August 2009, allow for the observations of local CO_2 emission impact on the level of this gas concentration observed at the mountain station.

Description of the Sampling Site

The measurement data discussed in this paper were obtained in KASLAB laboratory located in the building of the meteorological observatory at the top of Kasprowy Wierch, a mountain in southern Poland (1989 m asl). The observatory building is electrically heated, thus no emission is caused by the laboratory itself (excluding respiration of the crew members, usually consisting of one and rarely two observers). The only device inside the station building operating on liquid fuel is a diesel power generator installed in 2006 by IMGW employees. It is used as a reserve power supply for the station in the events of temporary power restrictions. These rare situations are well documented and all the measurement results are in this case excluded.

In the direct neighbourhood of the observatory there is a cable car station located about 30 m below the observatory. This building is also heated electrically. The equipment used for the measurements of greenhouse gas concentrations are in one of the observatory rooms, rented from the Institute of Meteorology and Water Management, Branch of Kraków, which owns the meteorological observatory building at Kasprowy Wierch and conducts a regular measurement program of meteorological parameters. The analyzed air is sucked through a heated inlet line derived approximately 1m above the roof of the observatory.

Kasprowy Wierch summit lies in the main ridge of the Tatra Mountains, about 400 m above the upper limit of the forest. It is surrounded by four valleys. The nearest town, Zakopane with almost 28,000 inhabitants, is located 6 km to the north and about one kilometre below Kasprowy Wierch. As this is the most famous mountain holiday resort in Poland, the number of people residing in the Podhale region increases by several factors during the summer and winter holidays. Zakopane and surrounding villages are dominated by low housing construction, and homes in the vast majority are still heated by coal or wood stoves. Therefore, in this region relatively large anthropogenic emissions of CO and CO_2 occur, especially during winter months.

Climate of the Tatra Mountains is a typical alpine temperate climate. An important phenomenon affecting the circulation of air is the temperature inversion in the lower troposphere (increase of air temperature with height) and the valley breeze winds. The inversion layer inhibits the vertical exchange of heat, water vapour, and other constituents of the atmosphere. Therefore, to determine equilibrium of the atmosphere it is critical in assessing the parameters of the transport of trace gases from the emission area to the measurement place.

Characteristic distribution of ridges and valleys for mountainous terrains contributes to significant changes in wind speed and direction in relation to the free atmosphere. Additionally, radiation heating and cooling of valleys and mountain slopes influence local wind circulation in the diurnal course. Such air movement is observed regularly over the Bystra Valley, where during the summer months an afternoon valley breeze blowing in the direction of Kasprowy Wierch at sunset is exchanged with the cool evening mountain breeze blowing in the opposite direction. Direction and wind speed in the Kasprowy Wierch region is affected strongly by the small-scale dynamics of the atmosphere, and thus also the concentrations of trace gases measured at the station remain under the influence of the strict neighbourhood.

The representativeness of atmospheric greenhouse gas concentrations measured at the Kasprowy Wierch laboratory is an extremely important parameter, however difficult to determine. The meteorological situation supporting the transport of locally emitted gases in the direction of the station should be described as accurately as possible.

Methods of Measurement

Measurement programs consisting of CO_2 and CH_4 concentration analyses in ambient air at Kasprowy Wierch was initiated in September 1994. At the beginning (until 1996) only average weekly air samples were collected. Also, several spot samples were taken and sent to a laboratory in Kraków. This type of measurement does not allow for analysis of short-term variability of atmospheric composition.

Since 1996, measurements of concentrations of major greenhouse gases (CO_2 and CH_4) at Kasprowy Wierch have been carried out by gas the chromatography technique. An automatic gas chromatograph (Hewlett Packard 5890) was equipped with a flame ionization detector, a 3 m long packed column (Porapak QS), and nickel catalyst converting carbon dioxide to methane. This method allows the measurement of carbon dioxide and methane with time repetition located in the range from several to tens of minutes, and a precision of 0.1 ppm and 2 ppb for CO_2 and CH_4, respectively.

The concentration of carbon monoxide in ambient air can also be determined chromatographically. The main advantages of the chromatographic method are high precision (~1 ppb) and low detection limit (~5 ppb). Analyses of atmospheric concentrations of CO at Kasprowy Wierch have been performed using a commercial device (Peak Performer PP1) since 2009. The PP1 analyzer consists of a gas chromatograph with RGD (reducing gas detector). The principle of operation of this detector is the reduction of mercury oxide vapors by carbon monoxide contained in the sample. Substrates of this reaction are vapors of metallic mercury that absorb ultraviolet radiation. A recorded decrease of UV intensity is proportional to the concentration of carbon monoxide in ambient air.

Results and Discussion

15 years of atmospheric measurements of CO_2 and CH_4 concentrations at Kasprowy Wierch allowed for a detailed analysis of temporal variation of the abundance of these gases in the atmosphere over Central and Eastern Europe [6-8, 16-18]. Measurements carried out at the station allowed us to determine of diurnal cycle, variability associated with mezzo-scale circulation, and possible fluctuations in long-term trends in concentrations of methane and carbon dioxide in the atmosphere over this part of Europe [7, 8].

Quasi-continuous measurements of atmospheric concentrations of methane and carbon dioxide carried out in the laboratory at Kasprowy Wierch provide 48 individually calibrated analyses daily. In the case of the time series analysis a daily mean concentration of both compounds often is used. These averages can be calculated in two ways:

(i) as the arithmetic mean of all measurements taken during the day

(ii) as average values calculated from the data selected in the process of filtering, based on accepted criteria [7, 16].

Such filtering is applied to remove all the data influenced by local effects (emissions from the immediate surroundings of the station) and affected by technical problems. Filtration procedures are usually applied in relation to measurements obtained from the so-called "clean" stations, situated in an undisturbed environment.

The diurnal averages of methane concentrations and carbon dioxide at the Kasprowy Wierch station during the period from September 1994 to December 2011 are presented in Fig. 1. All the data plotted on Fig. 1 were filtered and are supposed to represent regional data, free from local influences. This might be the basis for the analysis of long-term variability of methane and carbon dioxide concentrations in the atmosphere. Atmospheric CO_2 concentrations recorded at Kasprowy Wierch increased over 15 years of observation by approximately 30 ppm. Methane concentration has not increased in this period as substantially as CO_2. The average level of methane rose only by 30 ppb.

While Fig. 1 is suitable for seasonal and trend analysis, the diurnal cycle is not represented on this graph. On Fig. 2 the results of simultaneous measurements of CO and CO_2 concentrations at Kasprowy Wierch conducted from late August 2009 during one year are forming wide cloud of points aggregated along a seasonal trend. This graph presents all available unfiltered measurement data with relatively short periods (lasting up to several days), characterized by the simultaneous increase of the CO and CO_2 concentration. They indicate the occurrence of the relevant meteorological situations (e.g. the transition of atmospheric front) when station Kasprowy Wierch may be strongly influenced by local emissions of both gases.

The nearest city of Zakopane might be partially responsible for the elevation of carbon monoxide levels in the air over Kasprowy Wierch, especially on the diurnal timescale. A comparison of CO recorded at Kasprowy Wierch with daily average concentrations from Zakopane [14] is plotted on Fig. 3. The air in Zakopane city is characterized by relatively high concentrations of carbon

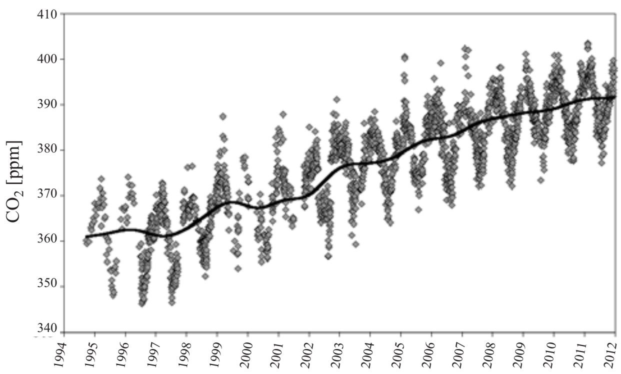

Fig. 1. Increase of carbon dioxide concentrations measured at the station Kasprowy Wierch. Until June 1996 the single points represented the average weekly concentrations of CO_2 in the atmosphere of Kasprowy Wierch. Later in the record, the individual points represent daily averages calculated on the basis of select data representing a regional signal, free from local influences from the immediate surroundings of the station.

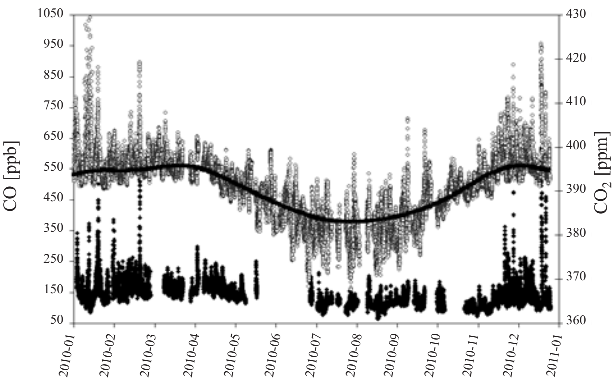

Fig. 2. Variations of carbon monoxide concentrations (black diamonds – left scale) and carbon dioxide (open circles – right scale) at the Kasprowy Wierch station, solid line – smoothed curve fitted to CO_2 concentration from the Kasprowy Wierch station. Points represents results of individual chromatographic measurements (none of the filtering or averaging data procedures applied).

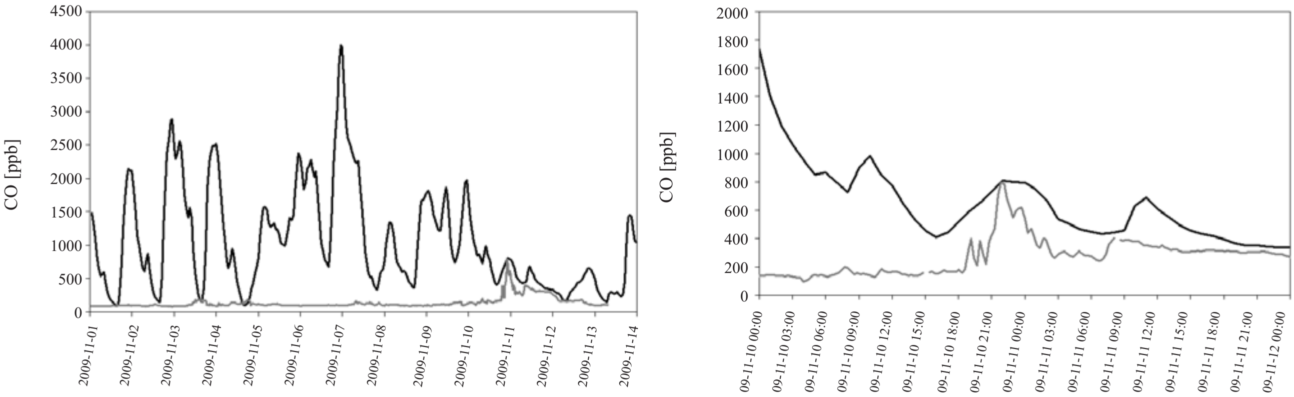

Fig. 3. Comparison of CO concentration variability in the atmosphere over Zakopane (black line) and at Kasprowy Wierch (grey line). Left panel presents the data from two weeks of measurements, the right panel represents carbon monoxide concentrations during two days included in the left panel.

monoxide (2000-2500 ppb), occurring mainly at night, related to the formation of the inversion layer.

Valley breezes frequently occurring in the area of Zakopane and Tatra are able to transport the air enriched in carbon monoxide from the area of Podtatrzański Trough (where the city is situated) toward the peaks of the Tatra mountains. Such situations are especially common during the summer season. In winter, during the period of weak breeze winds and strong temperature inversions, carbon monoxide present in the air of Zakopane can reach Kasprowy Wierch only during the specific meteorological situations described below:

(i) During the passage of atmospheric fronts or deep low pressure systems the air is in a state of unstable equilibrium, but the mixing height is significantly reduced. The nocturnal inversion layer is broken and the air is transported along the valley toward the peak areas. The concentrations of all gases observed at Kasprowy Wierch are rising significantly during the night and then decline gradually during the day, reaching a level of "background" after a few hours. Such a situation took place on 10 and 11 November 2009 (Fig. 4).

(ii) During high pressure circulation over the Podhale vertical equilibrium the state of the atmosphere is disabled during the morning hours by the appearance of breeze circulation associated with the observed strong temperature gradient during a bright day. Trace gas concentrations are rising gradually until the upslope currents are stopped and then fall sharply after reconstruction of the inversion layer. Such situations were observed on 9 and 10 of December 2009 (Fig. 5). The air coming over Kasprowy Wierch originally from the southeast is replaced by air flowing from the Podhale Trough (Fig. 5).

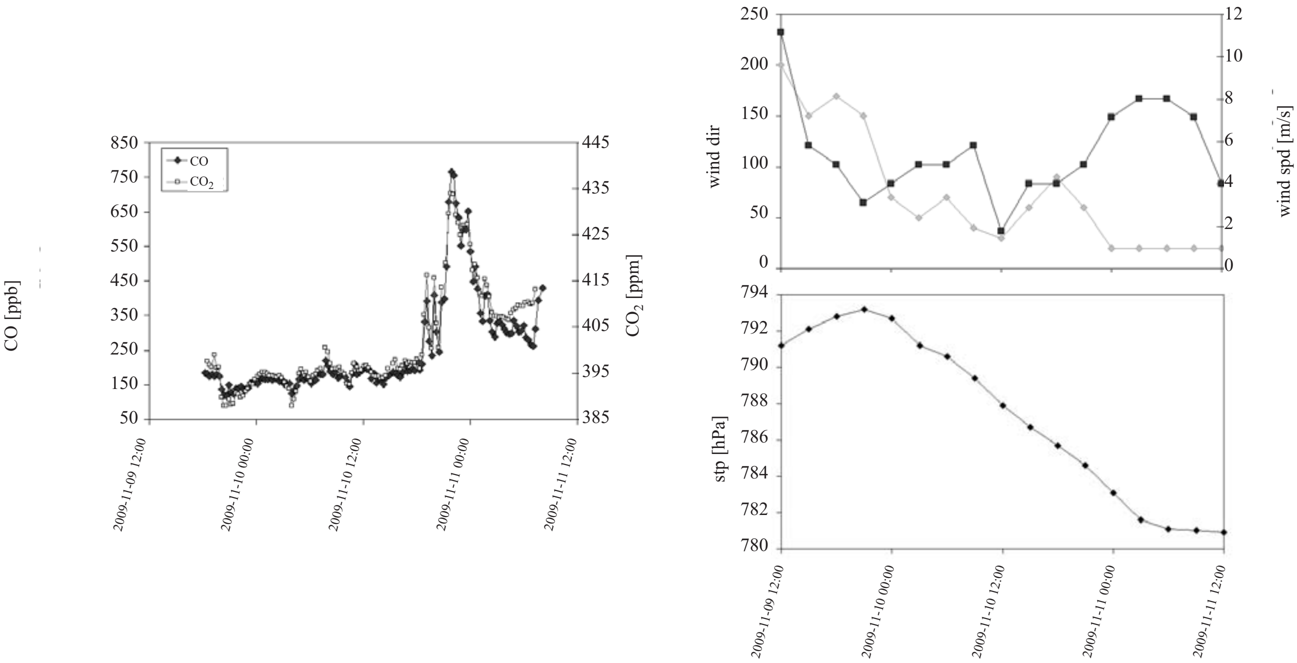

Fig. 4. An example of anomalously high concentrations of CO and CO_2 observed at the Kasprowy Wierch station on 10 and 11 November 2009. The left panel illustrates concentration variability of both gases. A record of wind speed and direction and barometric pressure during this period is shown on the right panel.

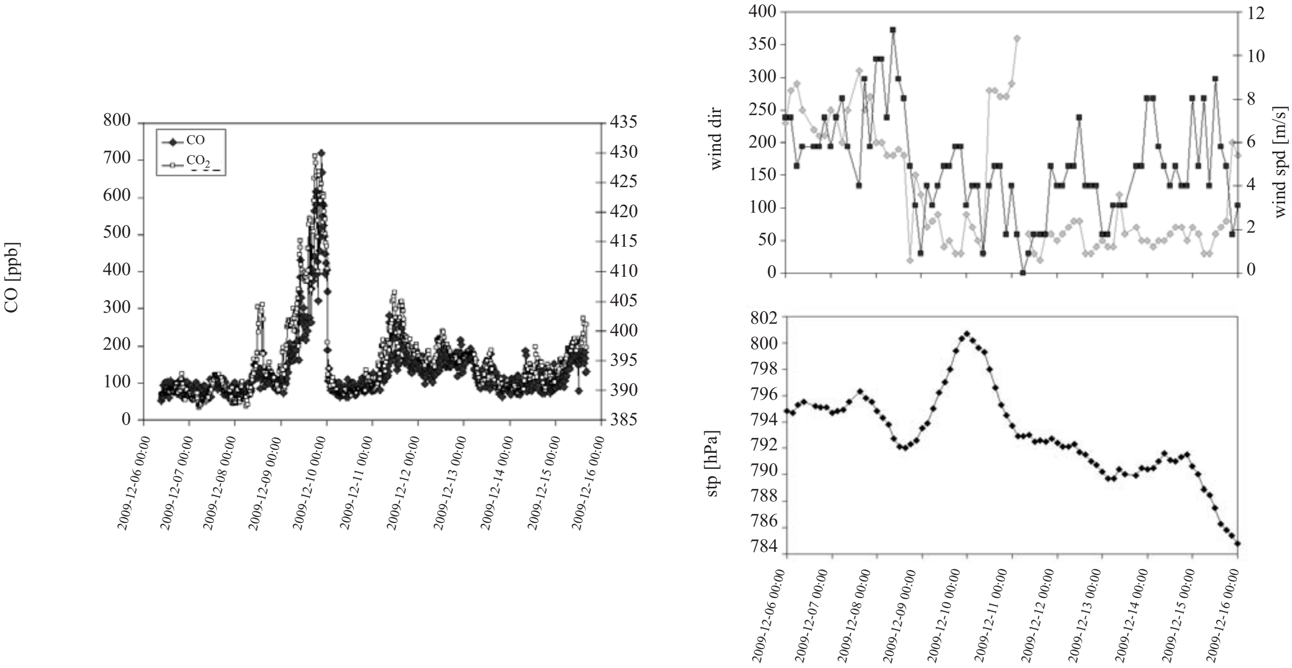

Fig. 5. An example of anomalously high concentrations of CO and CO_2 observed at the station Kasprowy Wierch on 9 and 10 December 2009. Left panel presents concentration fluctuations of both gas. Changes in wind speed and direction and barometric pressure during this period is illustrated on the right panel.

In both cases it is possible to estimate the impact of anthropogenic emissions of carbon dioxide on concentration levels of this gas measured at the station. CO_2 reaching the area of the Tatra mountains can be calculated by constructing a carbon dioxide balance:

$$C_{mix} = C_{bg} + C_{comb} + C_{resp} \tag{1}$$

...where:

C_{mix} – CO_2 concentration measured at Kasprowy Wierch

C_{bg} – carbon dioxide content in the background air

C_{comb} – contribution to CO_2 concentration derived from anthropogenic sources connected with combustion processes

C_{resp} – concentration of CO_2 coming from all other sources (e.g. processes of soil respiration).

Carbon dioxide concentrations C_{mix} are received directly from measurements. Background value C_{bg} may be obtained from measurements performed during nights that anticipated events of elevated CO concentration. Separation of the anthropogenic combustion component from the other sources is possible only with an additional marker. Typically, carbon isotope ^{14}C is used for this purpose [9, 19, 20] or carbon monoxide [21, 22]. The choice of relevant methodology depends on available measurements. In the case of Kasprowy Wierch measurements of radiocarbon concentration in atmospheric CO_2 are performed only using monthly integrated samples, mainly for economic reasons. Thus, carbon monoxide was used as an indicator of combustion process for the analysis of observed elevations of CO_2 mixing ratios in this study.

In both situations described earlier, the carbon monoxide concentration increased proportionally to the increase in CO_2 concentration (Fig. 6), but such proportionality occurs only occasionally. Slope coefficients were, within the error limits, identical (0.075 ppmCO_2/ppbCO). It cannot be explained only by carbon dioxide emissions from anthropogenic sources. The air free from CO emissions takes part in the mass balance as a significant component [6]. Mixed air containing both gases transported from the area of Zakopane to Kasprowy Wierch is a reason for the observed high ratio of CO_2 to CO concentrations. Carbon monoxide is formed only in the processes of incomplete combustion of biomass (e.g. wood) or fossil fuels (coal, petrol, natural gas, etc.). Combustion of fossil fuels in the most common low and medium power boilers produces CO_2 and CO at a ratio of approximately 30:1 [23, 24]. The use of wood as a fuel will introduce similar proportions of both gases.

During winter 2012 we performed direct measurements in Zakopane. The parallel measurements of CO and CO_2 during atmospheric stable conditions (11-13.02.2012) in two contrasting areas of the city were performed to check the applied assumptions. The inhabited part of the city without car traffic is located along the Biały Dunajec River. Measurements were performed while strong temperature inversion occurred, and accumulation of CO_2 and CO were purely visible from the results (Fig. 7). Additionally, stable isotope ^{13}C in carbon dioxide was determined. The correlation between $\delta^{13}C$ and inverse concentration leads to estimation of the isotopic signature of the CO_2 source. In this case value -22‰ was obtained indicating coal combustion as a main source of carbon dioxide over this area (Fig. 7 – right panel) [25].

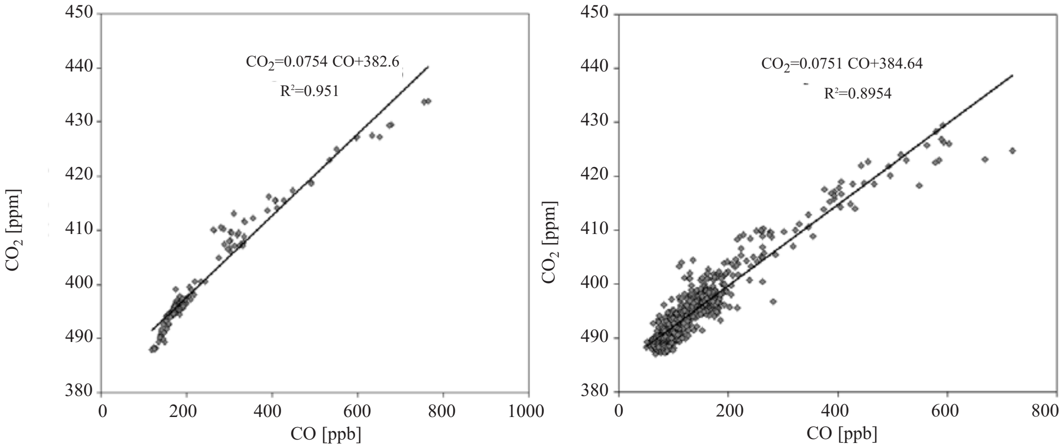

Fig. 6. CO_2 concentration in relation to the concentration of CO in ambient air observed at Kasprowy Wierch during the two anomalously cases, which occurred during November and December 2009.

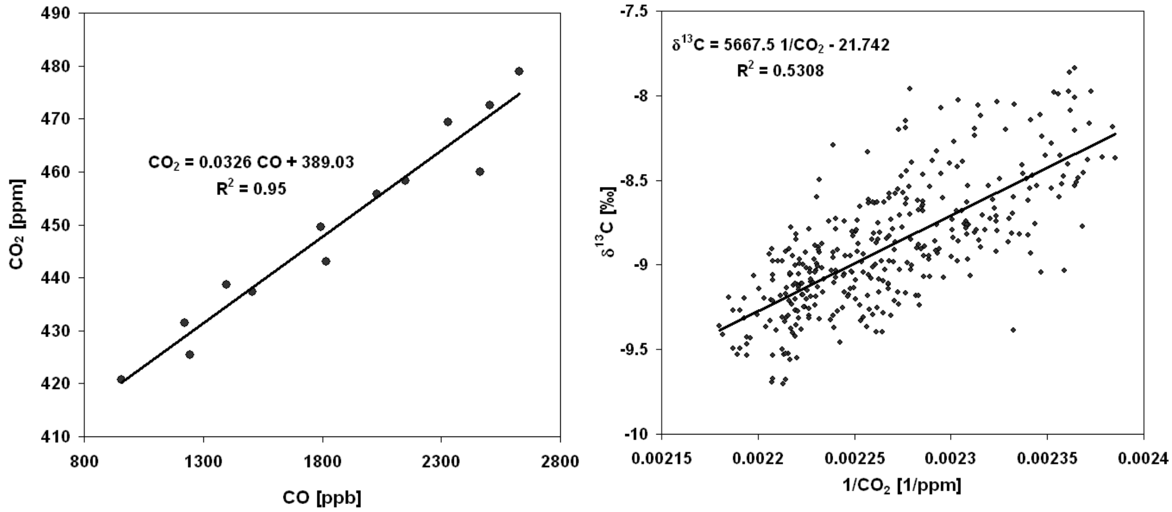

Fig. 7. Simultaneous emissions of CO and CO_2 from coal- and wood-burning furnaces derived from direct measurements performed over the living area of Zakopane in February 2012. The left graph illustrates CO_2/CO ratio. The right panel, the so-called "Keeling plot," presents the isotopic signature of CO_2 source at -22‰ (characteristic of coal incinerators).

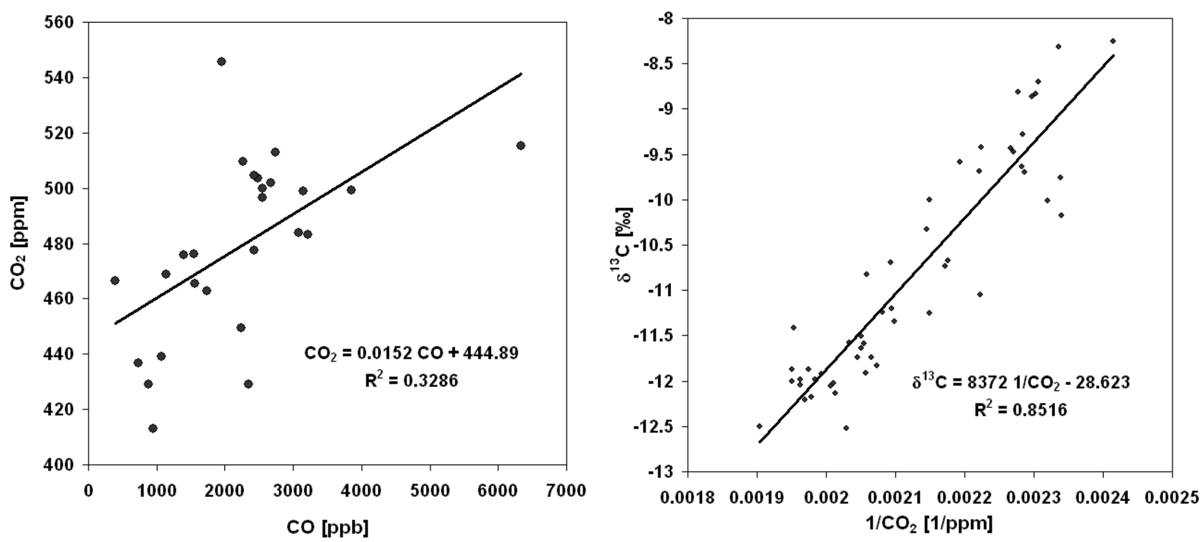

Fig. 8. Simultaneous emissions of CO and CO_2 from car exhausts derived from direct measurements performed along the roads with heavy car traffic in Zakopane in February 2012. The left graph illustrates CO_2/CO ratio. The right panel, or "Keeling plot," presents the isotopic signature of CO_2 source to -29‰ (characteristic of gasoline engines).

Automotive emission estimates for Poland leads to a ratio close to 15:1 CO_2/CO [26]. These data are subject to considerable uncertainty, and the range of variation often exceeds 100%. However, a measurement campaign conducted in heavy road traffic area of Zakopane confirmed this value (Fig. 8). Also, in this case determination of isotopic composition helped to ensure origination of CO_2 from car exhausts ($\delta^{13}C$ = 29‰). Assuming the relatively poor gasification of Zakopane, and additionally a 60% share of car traffic in total CO_2 emissions, we expected the average ratio between CO_2 and CO for anthropogenic combustion sources of 18:1. Available data from the Zakopane winter season campaign of 2012 delivered the overall average ratio in complete agreement with this assumption (Fig. 9). Measurement of CO concentration and the concentration of radiocarbon in atmospheric CO_2 in Kraków indicate the average ratio of 16:1 CO_2/CO in the winter [19]. A similar CO_2/CO relationship was observed in other European points where such measurements were applied [27]. Assuming the average CO_2/CO ratio for the emission from Zakopane area as 18:1, calculation of anthropogenic CO_2 contribution in the total concentration of this gas observed on Kasprowy Wierch was possible (Figs. 10 and 11). Components containing carbon dioxide from other sources was calculated from the balance equation (1).

As indicated in Fig. 10, the average level of the anthropogenic component of carbon dioxide at Kasprowy Wierch in the period under discussion was close to 2 ppm, with maximum values reaching 10 ppm. Contributions by other sources were characterized by a generally large variability, reaching a maximum of 35 ppm. Such a high level of respiratory and biological component can be explained by the relatively high air temperatures in this region during the winter period (circa 5ºC) and the complete lack of snow cover, which stimulates the processes of soil respiration [28]. Similar analysis carried out in other winter periods (January and February) during anomalous accumulations of CO_2 and CO concentrations with lower amplitude changes indicate a much smaller impact of soil respiration source of CO_2 in relation to the anthropogenic component.

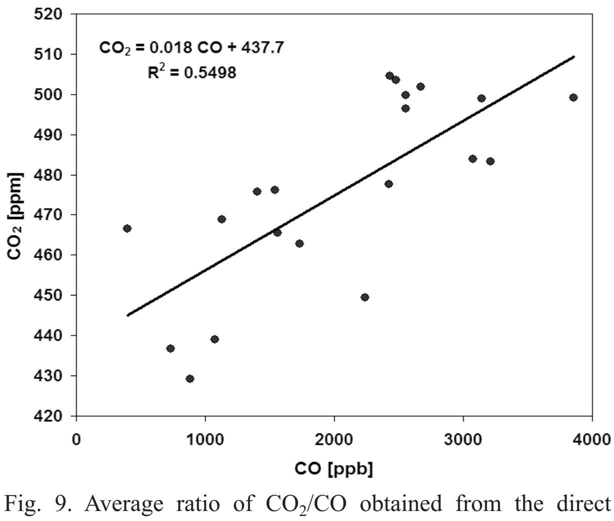

Fig. 9. Average ratio of CO_2/CO obtained from the direct atmospheric measurement campaign in Zakopane during the night 11/12.02.2012.

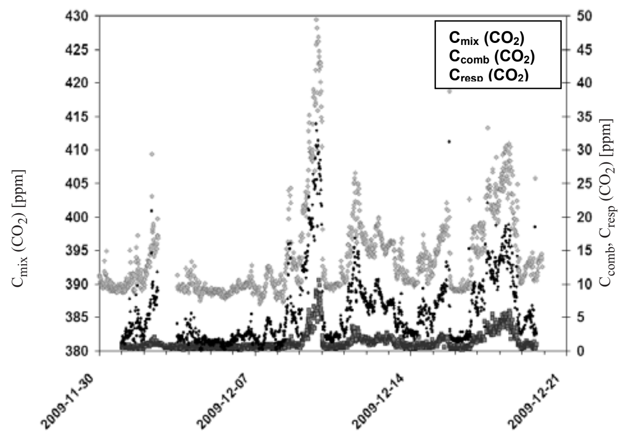

Fig. 10. Variation of CO_2 concentration in the ambient air on Kasprowy Wierch in December 2009. Grey diamonds show the measured concentrations of CO_2. Grey squares and black points show combustion and respiration components, respectively.

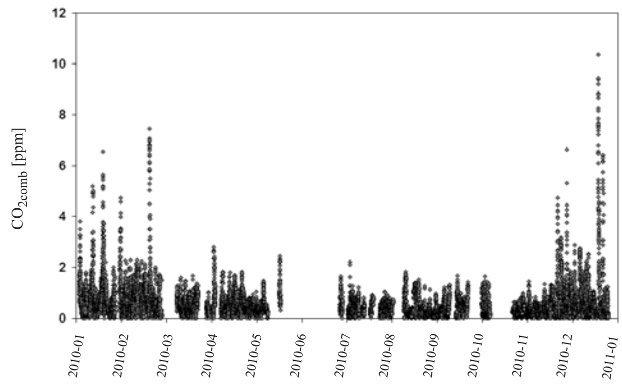

Fig. 11. Variation of estimated components of carbon dioxide originating from combustion sources over the Podhale area during the course of one year. Each diamond represents a single estimation half hourly value of CO_{2comb}.

The combustion component of CO_2 measured at Kasprowy Wierch reveals seasonal variation with maximum values observed in winter. The primary factor of this effect is coal and wood burning for house heating in the Podhale region. Even 10 ppm of CO_2 may originate from local emissions. During summer months car traffic remains intense and becomes a predominant source of the combustion component of carbon dioxide. In our calculation, the ratio of CO_2/CO was reduced to 15:1. On average only 0.5 ppm of measured CO_2 is coming from the local combustion sources during July and August (Fig. 11). This estimation is, however, only qualitative, and a large uncertainty (up to 100%) is connected with simplifications of the air transport from Podhale to Kasprowy Wierch. It is worth underlining that our estimation is working properly for specific meteorological conditions and a short period with sudden increase of abundance of both gases at Kasprowy Wierch.

Conclusions

Parallel observations of CO and CO_2 concentrations at Kasprowy Wierch are suitable for occasional estimation of the influence of local anthropogenic CO_2 emissions on its concentration level monitored at the station. While the inversion layer occurs, the abundances of both gases in Zakopane are increasing substantially. A similar situation occurs in Kraków [18] as well as other cities [29, 30]. For such cases, carbon monoxide can be used as a combustion tracer in simple balance of CO_2 at the Kasprowy station [10].

The combustion of wood, coal, and gasoline are introducing to the air CO in estimated relation to produced CO_2. The proportions of both gases were taken from the literature, but for particular cases were experimentally checked. Direct measurements performed in Zakopane city confirmed assumed CO_2/CO ratios for different sources and helped in partitioning carbon dioxide sources. Mass balance of both gases was constructed and used to determine the origins of carbon dioxide. Combustion sources over Podhale may be responsible even for 10 ppm of carbon dioxide abundance in the atmosphere at Kasprowy Wierch during winter pollution events. This is relatively low value in comparison to the estimates for bigger agglomerations [18]. In summer months the average levels of local combustion sources do not often exceed 1ppm, which is typical for remote mountain locations [31].

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References

1. IPCC – The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change Working Group I, S. SOLOMON et al. (Eds.) Cambridge University Press, Cambridge, **2007**.
2. LEVIN I., KARSTENS U. Inferring high-resolution fossil fuel CO_2 records at continental sites from combine $^{14}CO_2$ and CO observations, Tellus B, **59**, (2), 245, **2007**.
3. CIAIS P., PARIS J.D., MARLAND G., PEYLIN P., PIAO S.L., LEVIN I., PREGGER T., SCHOLZ Y., FRIEDRICH R., RIVIER L., HOUWELLING S., SCHULZE E.D. The European carbon balance: Part 1: Fossil fuel emissions. Glob. Change Biol. 16, 1395, **2010**.
4. LEVIN I., HAMMER S., KROMER B., MEINHARDT F. Radiocarbon Observations in Atmospheric CO_2: Determining Fossil Fuel CO_2 over Europe using Jungfraujoch Observations as Background. Sci. Total Environ. **391**, (2-3), 211, **2008**.
5. RIVIER L., CIAIS P., HAUGLUSTAINE D. A., BAKWIN P., BOUSQUET P., PEYLIN P., KLONECKI A. Evaluation of SF6, C2Cl4 and CO to approximate fossil fuel CO_2 in the Northern Hemisphere using a chemistry transport model. J. Geophys. Res. **111**, D16311, doi:10.1029/2005JD006725, **2006**.
6. CHMURA L., RÓŻAŃSKI K., NĘCKI J.M., ZIMNOCH M., KORUS M., PYCIA M. Atmospheric Concentration of Carbon Dioxide In Southern Poland: Comparison of Mountain and Urban Environments. Pol. J. Environ. Stud. **17**, (6), 859, **2008**.
7. CHMURA L. Greenhouse gases in atmosphere of southern Poland: Spatial and temporal variability (years 1994-2007). PhD thesis, faculty of Physics and Applied Computer Science, Kraków, **2009** [In Polish].
8. CHMURA Ł., NĘCKI J., ZIMNOCH M., KORUS A., RÓŻAŃSKI K., MILANÓWKA D., KARZYŃSKI M. Fifteen years of greenhouse gases measurements at high mountain meteorological observatory Kasprowy Wierch. Tatry TPN No.4 Special Edition, **2009** [In Polish].
9. KUC T. Concentration and carbon isotopic composition of atmospheric CO_2 in southern Poland. Tellus B **43**, (5), 373, **1991**.
10. GAMNITZER U., KARSTENS U., KROMER B., NEUBERT R., MEIJER H., SCHROEDER H., LEVIN I. Carbon Monoxide: A quantitative tracer for fossil fuel CO_2. J. Geophys. Res., **111**, D22302, doi:10.1029/2005JD006966 **2006**.
11. TURNBULL J. C., MILLER J. B., LEHMAN S. J., TANS P. P., SPARKS R. J. SOUTHON J. Comparison of $^{14}CO_2$, CO, and SF6 as tracers for recently added fossil fuel CO_2 in the atmosphere and implications for biological CO_2 exchange. Geophys. Res. Lett., **33**, L01817, doi:10.1029/2005GL024213, **2006**.
12. NOVELLI P. C., MASARIE K. A., LANG P. M., HALL B. D., MYERS R. C., ELKINS J. W. Reanalysis of tropospheric CO trends: effects of the 1997-1998 wildfires. J. Geophys. Res. **108**(D15), 4464, doi:10.1029/2002JD003031, **2003**.
13. RÖCKMANN T., BRENNINKMEIJER C.A.M., SAUERESSIG G., BERGAMASCHI P., CROWLEY J., FISCHER H., CRUTZEN P.J. Mass independent fractionation of oxygen isotopes in atmospheric CO due to the reaction CO + OH. Science **281**, 544, **1998**.
14. WIOS Krakow department, elaboration: "Five-yearassessment ofair qualityin terms of pollution with: SO_2, NO_2, NO_x, CO, C_xH_x, O_3, particulate matter PM_{10}, and As, Cd, Ni, Pb and BaP in Lesser Poland province," **2010** [In Polish].
15. GLOBALVIEW-CO: Cooperative Atmospheric Data Integration Project – Carbon Monoxide. CD-ROM, NOAA ESRL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co/GLOBALVIEW], **2009**.
16. NECKI J.M., SCHMIDT M., ROZANSKI K., ZIMNOCH M., KORUS A., LASA J., GRAUL R., LEVIN I. Six-year record of atmospheric carbon dioxide and methane at a high-altitude mountain site in Poland. Tellus, **55B**, 94, **2003**.
17. NĘCKI J.M. Estimation of Greenhouse gas emission in Local and continental scales using the datafile from measurement station at Kasprowy Wierch. PhD Thesis. faculty of Physics and Applied Computer Science, Kraków, **1998** [In Polish].

18. ZIMNOCH M., JELEN D., GALKOWSKI M., KUC T., NECKI J.M., CHMURA L., GORCZYCA Z., JASEK A., ROZANSKI K. Partitioning of atmospheric carbon dioxide over Central Europe: insights from combined measurements of CO_2 mixing ratios and their carbon isotope composition. Isot. Environ. Healt. S. **48**, (3), 421, **2012**.
19. KUC T., ROZANSKI K., ZIMNOCH M., NECKI J., CHMURA L., JELEN D. Two Decades of Regular Observations of $^{14}CO_2$ and $^{13}CO_2$ Content in Atmospheric Carbon Dioxide in Central Europe: Long-Term Changes of Regional Anthropogenic Fossil CO_2 Emissions. Radiocarbon, **49**, (2), 807, **2007**.
20. RAKOWSKI A., PAZDUR A., NAKAMURA T., PIOTROWSKA N., Variations of anthropogenic carbon dioxide in urban area deduced by radiocarbon concentration in modern tree rings. Geophysical Research Abstracts **12**, EGU2010-2152, **2010**.
21. GROS V., JÖCKEL P., BRENNINKMEIJER C.A.M., RÖCKMANN T., MEINHARDT F., GRAUL R. Characterization of pollution events observed at Schauinsland, Germany, using CO and its stable isotopes. Atmos. Environ. **36**, (17), 2831, **2002**.
22. LEVIN I., RÖDENBECK C. Can the envisaged reductions of fossil fuel CO_2 emissions be detected by atmospheric observations? Naturwissenschaften **95**, (3) 203, **2008**.
23. NICKS JR D. K., HOLLOWAY J. S., RYERSON T. B., DISSLY R. W., PARRISH D. D., FROST G. J., TRAINER M., DONNELLY S. G., SCHAUFFLER S., ATLAS E. L., HUBLER G., SUEPERA D. T., FEHSENFELD F. C. Fossil-fueled power plants as a source of atmospheric carbon Monoxide. J. Environ. Monit. **5**, 35, **2003**.
24. PN-EN 12809, Polish standard "Boilersfired by solid fuel.Nominalheat output up to50kW.Requirements and test methods" [In Polish].
25. ZIMNOCH M. Stable isotope composition of carbon dioxide emitted from anthropogenic sources in the Kraków region, Southern Poland, Nukleonika, **54**, (4), 291, **2009**.
26. RYMASZEWSKI E. Elaboration titled "Exhaust gas analysis in engine with spark ignition" Motor Vehicle Engineering High School in Bydgoszcz, **2010** [In Polish].
27. GAMNITZER U., KARSTENS U., KROMER B., NEUBERT R.E.M., MEIJER H., SCHROEDER H., LEVIN I. Carbon monoxide: A quantitative tracer for fossil fuel CO_2?, J. Geophys. Res., **111**, No. D22, D22302 10.1029/2005JD006966, **2006**.
28. SOGACHEV A., LECLERC M.Y., ZHANG G., RANNIK Ü., VESALA T. CO_2 fluxes near a forest edge: a numerical study. Ecol. Appl., **18**, (6), 1406, **2008**.
29. VESALA T., JÄRVI L., LAUNIAINEN S., SOGACHEV A., RANNIK Ü., MAMMARELLA I., SIIVOLA E., KERONEN P., RINNE J., RIIKONEN A., NIKINMAA E. Surface-atmosphere interactions over complex urban terrain in Helsinki, Finland, Tellus B **60**, (2), 188, **2008**.
30. SCHULZE E. D., CIAIS P., LUYSSAERT S., SCHRUMPF M., JANSSENS I. A., THIRUCHTTAMPALAM B., THELOKE J., SAURAT M., BRINGEZU S., LELIEVELD J., LOHILA A., REBMANN C., JUNG M., BASTVIKEN D., ABRIL G., GRASSI G., LEIP A., FREIBAUER A., KUTSCH W., DON A., NIESCHULZE J., BÖRNER A., GASH J., DOLMAN A. J. The European carbon balance. Part 4. Integration of carbon and other trace gases fluxes. Glob. Change Biol. **16**, 1451, **2010**.
31. ENEROTH K., AALTO T., HATAKKA J., HOLMÉN K., LAURILA T., VIISANEN Y. Atmospheric transport of carbon dioxide to a baseline monitoring station in northern Finland. Tellus B **57**, (5), 366, **2005**.