

Interactive comment on “Atmospheric concentrations of carbon dioxide and its isotopic composition in southern Poland: comparison of high-altitude mountain site and a near-by urban environment” by L. Chmura et al.

Anonymous Referee #2

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L. Chmura, K. Rozanski, J. M. Necki, M. Zimnoch, T. Kuc, and A. Korus Atmospheric concentrations of carbon dioxide and its isotopic composition in southern Poland: comparison of high-altitude mountain site and a near-by urban environment

General comments

The manuscript falls within the scope of BG. It presents a unique geophysical dataset, which for some parts is the continuation of a longer record (e.g. ^{14}C in Krakow), making it even more interesting for the detection of longterm changes. The conclusions, however, are very general and taken from the data set only in a very rough and qualitative way. There is no single effort visible to quantify the suggested effects and mechanisms

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leading to the observed records, or at least show their technical possibility by some basic mass balance estimations. Cited and discussed records from other (clean air) monitoring stations are not shown for comparison and as an (at least visual) proof of the given thesis. The working principles and thus usefulness of the isotope data is not revealed sufficiently.

In first instance there is no doubt that the data will support the conclusions, but it still urgently needs to be shown first that:

” Carbon isotopic composition of atmospheric CO₂ proved to be an efficient tool for identification the surface CO₂ fluxes into the atmosphere related to fossil fuel burning, their strength and temporal variability, as well as their influence on the recorded levels of this gas in the local atmosphere.”

Once really supported by the data and quantified, the abstract and conclusions will be more detailed and to the point than they are now. The structure is clear, and could be improved in minor details only (see below). Some items should be explained by a few more words, as suggested in the specific comments. In general, it is desirable that the authors write less in general terms and expressions, also concerning numbers like e.g. annual averages and their derivation. This might lead to some more references.

Quantification of the addressed effects (e.g. the amount of fossil fuel CO₂ in Krakow air) is necessary before publication.

Specific comments

Abstract:

1850/8; the relative proximity is given only in a horizontal sense, don't forget the (already mentioned) 1800 m height difference.

1850/12; unfortunately only very general facts (“was almost 10% higher”) can be given here, as no more detailed conclusions are deduced later in the manuscript. More details are needed, e.g. differences during diurnal cycles, the annual cycle, time lags

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etc.

1850/14; “Carbon isotopic composition of atmospheric CO₂ proved to be efficient tool for identification the surface CO₂ fluxes intoĚ” This is only discussed very roughly and qualitatively in the manuscript, not even an estimation of the quantity of fossil fuel-derived CO₂ is given.

1850/23; Cite IPCC rather than Globalview. The latter is a data product, whereas the first discusses the interpretation of the data.

1851/1; add “to or from the land biosphere and the world oceans.” at the end of the sentence.

1851/14-20; the economic transition in Eastern Europe started around 1990. If it is to show the effects of this transition, data from before this time should be taken into account and compared to the latest data wherever possible.

1851/ 27; Don't forget the 1800 m height distance.

1852/16; Is there any (local) topographic reason for winds blowing predominantly along N-S directions in a region that frequently experiences westerly winds, as you state for Krakow later on?

1852/18; which are the winter months (fromĚtoĚ)? Is there a difference in the northern vs. the southern part of the surroundings due to the föhn influences (e.g. cold and wet to the south, warm and dry to the north of the main tatra mountains ridge)?

1853/25; which version of the WMO CO₂ mole fraction scale do you apply? In fall 2005 a new version (2005X) has been released, eventually deviating considerably from earlier versions.

1854/27 and 1855/3; It is not clear when the maximum appears. In January - February, ending in March is very broad and general.

1855/3-5; is there any meteorological evidence for the pollution coming up from Za-

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kopane?

1855/5-7; how is the peak-to-peak amplitude computed? Which data (pollution events?) are included, which are not? Is there any data selection procedure you apply?

1855/8; same question for the annual averages: any data selection applied?

1855/8; an increase of 20 ppm within seven years translates into almost 3 ppm per year on average, whereas most other stations see about 1.5 ppm/year. Do you see any explanation for this effect?

1855/8; “The CO₂ levels recorded in Krakow are generally higher (around 440 ppm in 2004)” does not fit in my view with “The annual average CO₂ concentration in 2004 recorded at Kasprowy Wierch was equal 378 ppm while in Krakow it reached 408 ppm.” What do the two different numbers for Krakow tell us?

1856/19-20; “The offset of Krakow 13C record with respect to maritime reference station Mace Head is even higher”: Please show the reference data.

1857/3ff; show the continental reference (background) record

1857/15; explain the meaning of “low emission”.

1857/17; “E. characterization of spatial and temporal variability” Until now it’s more a display rather than a characterization.

1858/10-13; “Carbon isotopic composition of atmospheric CO₂ proved to be an efficient tool for identification the surface CO₂ fluxes into the atmosphere related to fossil fuel burning, their strength and temporal variability, as well as their influence on the recorded levels of this gas in the local atmosphere.”

The influence of urban CO₂ sources can not be overlooked, and 14C is showing the fossil nature of (part of) the sources. However, even if the conclusions you draw surely will be right in the end, they are not yet in any quantitative way or by any rough esti-

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mation supported by your nice dataset. A few ideas about simple mass balances to estimate are given below.

1862/Fig.2; it's impressive to see the full record with all local peaks, but the concentrations around the background (e.g. for Kasprowy station from the lowest value up to 390 ppm) must be zoomed into. In order to make comparison possible, e.g. the lower envelope of the Kasprowy curve or a running mean after data selection (for free tropospheric air) should be defined and appear in the Krakow data record as a reference. The appropriate Globalview data (e.g. latitude's marine background) would be another good choice to be included in the figures to show the continentality of and local human influences at the stations.

1863/Fig.3; a: indicate the date if it has been one single day (the same day for both stations I guess), or otherwise state which period you averaged. Please give the meteorological conditions for this typical situation.

1863/Fig.3; b: please include the marine background into the graph. Also here it would be interesting to zoom in to the concentration range at Kasprowy (including the background) to judge the continentality of the station (i.e. the biospheric CO₂ concentration drawdown).

1864/Fig. 4; Please include a few typical uncertainty ranges for the Krakow data, they are probably dependent on the difference to the Kasprowy data. It would be interesting to see the daily minimum value at Krakow. Like in the zoomed-in graph of Fig. 3b it should be visible if there is a daily period of well-mixed conditions (like in Fig. 3a) or not.

1865/Fig. 5; a: Krakow shows very distinct seasonal cycles, whereas Kasprowy only shows a slow decrease of the 14C-content. In order to make a computation of the fossil fuel CO₂-load, you need to compare the signal to the continental background (e.g. Jungfraujoch). If you want to draw conclusions about the change of fossil fuel production since the start of the economic changes, you should explicitly go back

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to the 14C-data of the late 80's and early 90's of the last century. At least the fossil fuel load at Krakow as compared to Kasprowy can and should be deduced from the records.

1865/Fig. 5; b: As you write in the text, the Kasprowy and Krakow 13C-data approach the background values of e.g. Mace Head. It is even very amazing how fast this happens in the years under examination. The trend is not at all small (as is written at 1856/22), being about +1 permil within 4 years, compared to about -0.2 permil at Mace Head (NOAA-CMDL data). The Kasprowy and Mace Head records almost touch each other during winter time, while in summer there is a difference of about 2 permil. This implies that next to the opposite trend, also the phase is reversed between the records. Please show by a short mass balance estimation what the $\delta^{13}C$ of the additional CO₂ at Kasprowy (and Krakow) is. Knowing the fossil fuel contribution from the data in Fig. 5a (and the continental background) you can even find the $\delta^{13}C$ of the fossil fuel-derived CO₂. The formalism has a.o. been given by Meijer, H. A. J., H. M. Smid, E. Perez, and M. G. Keizer, 1996: Isotopic characterisation of anthropogenic CO₂ emissions using isotopic and radiocarbon analysis. *Phys. Chem. Earth*, 21, 483–487.

Maybe the fitting procedure, which emphasizes annually repeated structures, is not the best for the dataset in question as this is not real “clean air”. From the concentration differences in the respective two-weeks period and the differences in $\delta^{13}C$ you can come to an estimation of the $\delta^{13}C$ of the source CO₂ (Krakow relative to Kasprowy). There might be annual variations according to the mix of the sources (heating vs. industry vs. mining vs. car traffic). In both Fig. 5a and b the clean air records must be included (Jungfraujoch and Mace Head resp.).

Technical corrections

The manuscript should be checked by a native english speaker or other language expert, especially for articles to be added in order to make the reading more fluent.

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1850/21; “Abrupt over the last 100 years” might not be the best wording for the known phenomenon.

1853/11; “and frequent temperature inversion situations,”

1853/19; mention the column first, then the detector.

1854/2; “sampled by adsorption”

1854/6; “by stable isotope mass spectrometry (give the manufacturer and type of the mass spectrometer).”

1854 ff chapter 4: Either in subtitles or more clearly in the text you might state the sub-topic under discussion: trend / seasonal cycle / diurnal cycle / daily mean.

1854/17; should read Krakow.

1858/19; should read CARBOEUROPE-IP

P.S.: In case that my comments appear to be unclear, please don't hesitate to ask for more explanations. Unfortunately underlining and italics are not supported in the non-LateX mode, and even Line feed / Carriage returns disappear in the pdf version!

Interactive comment on Biogeosciences Discussions, 2, 1849, 2005.

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