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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of CO_2, its stable isotopes, O_2/N_2, and ^{222}Rn at Bern, Switzerland" *by* P. Sturm et al.

Anonymous Referee #1

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General comments: This paper presents a very useful data set of concentrations and isotope measurements of atmospheric compounds in an urban environment. Method tests are performed to investigate thermal fractionation at the air inlet. Diurnal and seasonal patterns of CO2 and its isotopes are characterized and combined with 222Rn measurements to estimate a mean CO2 flux density. The combination of the presented set of different atmospheric tracers is novel and deserves publication in ACPD. However, my main reservation is that the paper is somewhat unbalanced regarding technical versus interpretational aspects. The part on thermal diffusion and inlet fractionation is explained in great detail, with corresponding results referring to figures 2-5, while on the other hand later parts of the results and discussion section remain some-

what sketchy and preliminary, e.g. what the observed O2/CO2 ratios could mean and how reliable this calculation is, how well the CO2 flux density estimations compare with other independent measures etc. I think that it would be possible to prepare a separate short paper on technical aspects to be submitted, for an instance, to Rapid Comm. Mass. Spectr. This part could then be removed from the present paper and make the manuscript much more focused. Even if this separation does not seem feasible to the authors, significant improvement and expansion of the discussion part is required before this manuscript becomes acceptable for publication in ACPD.

Detailed comments: 1) Abstract: Indicate rather the time-resolution than speaking of ”continuous” measurements which is unclear (could in principal be anything from seconds to minutes to hours)

2) Methods: Why is a N2O correction applied to the isotope measurements? Is there not a GC used to separate N2O from CO2?

3) Temperature-dependent fractionation at the inlet: A lab experiment could have been useful to verify temperature-dependent fractionation at tees

4) Regarding the slope of the correlation plot of Ar/N2 versus O2/N2 (3.8ś0.1, Fig. 5a): It is stated that it is in ”good accordance” with what is expected from thermal fractionation according to Grew and Ibbs, 1952 and Keeling et al., 2004. This should be explained in more detail rather than just pointing the reader to these references. How well do the results compare?

5) Strong variations are observed in the Keeling-plot derived source isotope values, in particular for 18O of CO2. Some tentative explanations are given, e.g. the exchange with plants. I would assume, however, that the high CO2 concentrations in winter are mainly caused by combustion sources, and that thus the exchange with the biosphere cannot be the reason for the highly variable results. Mixing models are mentioned but not applied. A prerequisite for understanding the variations would also be to include climatic conditions.

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6) The proposed explanations for the observed O2/CO2 oxidation ratios are not satisfactory (e.g. ”biogenic sink up to four times as strong as the fossil fuel source”, ”overestimation of the span of our scale by more than 10%”). It is not clear whether the observed variations are unrealistic, or whether only the explanations are unclear. In any case, the interpretation is very preliminary

7) Thermal diffusion effects again are important for d29N2, d34O2 and d36Ar. How much of the observed variation is real? The discussion of the results is rather short and inconclusive

8) The 222Rn exhalation rate and the CO2/222Rn slope are quite uncertain, thus the estimated CO2 flux density should be compared with some independent measures of CO2 emissions or some other studies from the literature (e.g. eddy-flux measurements). At least the fossil fuel combustion can be estimated from inventories for the region under investigation and may provide some basic comparison for winter conditions.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 8473, 2005.