EVALUATION OF CO AND SF_6 AS QUANTITATIVE TRACERS FOR FOSSIL FUEL CO_2: THE EXPERIMENTALISTS' VIEW

I. Levin[1], U. Gamnitzer[1], U. Karstens[2], Ch. Schönherr[1], B. Kromer[1], and S. Hammer[1]

[1]*Institut für Umweltphysik University of Heidelberg, INF 229, D-69120 Heidelberg, Germany; ilevin@iup.uni-heidelberg.de,ugamnitz@wzw.tum.de,cschoen@iup.uni-heidelberg.de, bkromer@iup.uni-heidelberg.de,shammer@iup.uni-heidelberg.de*

[2]*Max-Planck-Institute for Biogeochemistry, Hans-Knöll-Str. 10, D-07745 Jena, Germany, karstens@dkrz.de;*

ABSTRACT

Three years of quasi-continuous atmospheric $^{14}CO_2$ observations in Heidelberg (Germany) have been used together with continuous CO measurements to determine the CO/fossil fuel CO_2 ratio in a regional polluted area. Comparison with bottom-up information on fossil fuel CO_2 and CO emissions for the respective catchment area shows that large discrepancies (up to 60%) between inventory data and observations exist. Therefore both, a lot of care and reliable emissions inventory data are necessary if CO shall be used as a quantitative surrogate for fossil fuel CO_2.

INTRODUCTION

Fossil fuel CO_2 emissions play a major role in the European carbon budget. About half of the additional continental atmospheric CO_2 signal (relative to background air) observed at urban but also at more remote sites in Europe is caused by regional fossil fuel CO_2 emissions. Accurate quantitative knowledge of the fossil fuel component is, therefore, crucial to assess e.g. the role of the continental biosphere as a net source or sink of carbon by atmospheric observations and inverse modelling. The $^{14}C/^{12}C$ ratio in atmospheric CO_2 provides the only quantitative measure of the fossil fuel CO_2 component. However, quasi-continuous observations of $^{14}CO_2$ are, at present, too sparse and do not provide the temporal resolution needed to serve for reliable validation of model results all over Europe. A number of surrogate tracers for fossil fuel CO_2, such as CO or SF_6, have been suggested and used in the past to quantify fossil fuel CO_2 and to replace the sophisticated and expensive atmospheric $^{14}CO_2$ observations. Application of these tracers on the regional scale is discussed here.

RESULTS

Continuous half-hourly CO_2, CO, SF_6 and ^{222}Radon observations in Heidelberg are shown in Figure 1 for a five days period in autumn 2004. While CO_2 and ^{222}Radon have similarly distributed and more or less homogeneous area sources, emissions of CO (mainly from traffic) and SF_6 (industrial sources or electric power stations) are distributed heterogeneously or are even released from single point sources. These source characteristics are mirrored in the respective mixing ratio variability at our sampling site in the outskirts of Heidelberg (University campus) about 25m above local ground. CO_2 and ^{222}Radon variations correlate very well, and are, thus, driven mainly by boundary layer mixing. CO generally follows the same pattern. For example, on Sept. 30, 2004, CO shows two distinct rush hour peaks which are also well developed in the CO_2 record, but the ratio between the CO and CO_2 "bumps" changes during the day because CO_2 has also large biogenic sources, as well as from day to day. For SF_6 we frequently observe large peaks originating from single point sources, but this component also exhibits some similitude with the other trace gases; this behaviour is, however, strongly dependent on wind direction. From this simple qualitative comparison we can already conclude that the non-co-location of SF_6 and fossil fuel CO_2 emissions is a serious obstacle to using SF_6 as a surrogate tracer, at least on the regional scale (10 to 100 km).

Monthly mean night-time $^{14}CO_2$ measurements in Heidelberg are shown in Figure 2a in comparison with the continental $^{14}CO_2$ background derived from Jungfraujoch observations [*Levin and Kromer*, 2004]. The regional fossil fuel CO_2 component (Fig. 2b) is calculated from these data according to Levin et al. [2003] and compared to the regional CO offset, ΔCO, compared to the background level (Fig. 2c). There is a striking correlation between the fossil fuel CO_2 component and the monthly mean CO offset in Heidelberg. The mean ratio is determined to (14±3) ppb CO/ppm CO_2(foss) which is higher by 17% (EDGAR [*Olivier and Berdowski*, 2001]) and 61% (IER emission data, Dec. 21, 2004, http://carboeurope.ier.uni-stuttgart.de) compared to the mean values derived from the respective inventories in the 100km x 100km area west of Heidelberg. This discrepancy may have several reasons: CO is not a conservative tracer but has atmospheric sinks and sources other than fossil fuel emissions, which need to be taken into account here (compare accompanying paper by *Karstens et al.*, this issue). Similarly important, the catchment

area of Heidelberg is probably much larger than the 100km x 100km grid, and our observations surely include influence from source areas with higher CO/CO_2(foss) ratios, for example in France.

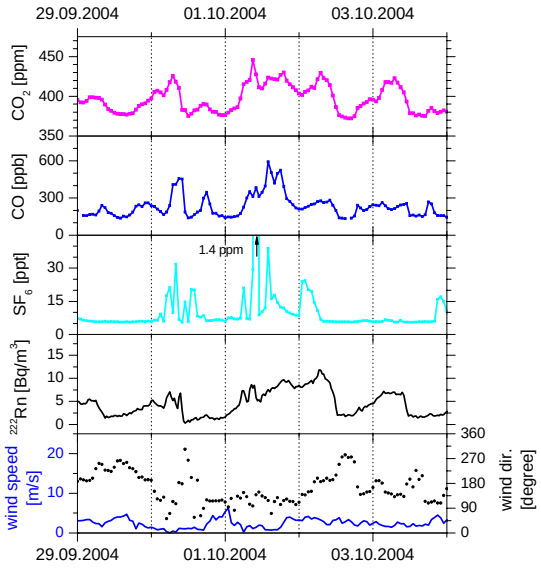

Fig. 1: Continuous observations of CO_2, CO, SF_6, ^{222}Radon and wind data (solid line: velocity) in Heidelberg. While there is a very good correlation between CO_2 and CO, SF_6 shows much more variability caused by emissions from point sources

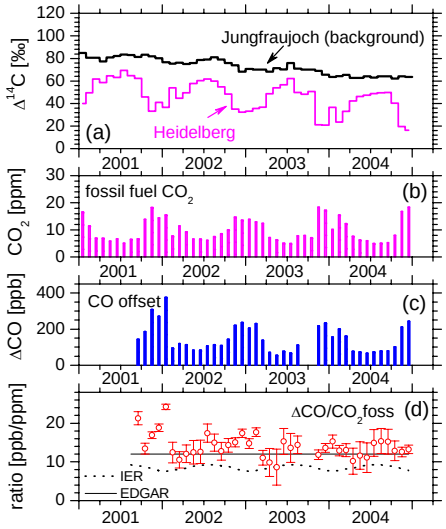

Fig. 2: Monthly mean $^{14}CO_2$ (a), ^{14}C-derived fossil fuel CO_2 (b) and CO offset to background (c) observations in Heidelberg. The ratio between ΔCO and fossil fuel CO_2 is plotted in (d) together with mean values from emissions inventories for the 100km x 100km grid west of the sampling site

CONCLUSIONS

Our study shows that on the regional scale and integrated over two weeks, the fossil fuel CO_2 component correlates well with the respective CO offset. This is an important prerequisite if CO shall be used as a surrogate tracer to determine the fossil fuel CO_2 component. The accuracy of the CO tracer method is, however, strongly dependent on the accuracy of the emissions inventory and its ability to correctly represent the ratio of CO/CO_2 in the fossil fuel emissions. This difficult task has obviously not yet been fully accomplished in the available inventories. Therefore, for any observational site where the CO tracer method shall be applied, a proper validation of the underlying emissions inventories, e.g. with $^{14}CO_2$ measurements, is necessary. At a regional polluted site this validation is more reliable because the fossil fuel CO_2 signals are large enough to achieve precise (±10% error) results. However, at more remote stations such as Schauinsland the fossil fuel CO_2 signals become quite small (on the order of only 1-2 ppm corresponding to about 2-5 ‰ $\Delta^{14}C$ signal [*Levin et al.*, 2003]), and validation by using $^{14}CO_2$ will be less reliable. In the case of SF_6, which has the advantage to be chemically stable in the atmosphere, contrary to CO with an atmospheric life time of only a few months, the situation is complicated because its sources are not co-located with fossil fuel CO_2. However, at remote stations, where the heterogeneity of SF_6 emissions is smoothed out by atmospheric mixing, this tracer may be better suited than CO, if proper validation of its emissions inventories can be achieved.

REFERENCES

Levin, I., Kromer, B., Schmidt, M., Sartorius, H. (2003), A novel approach for independent budgeting of fossil fuels CO_2 over Europe by $^{14}CO_2$ observations. *Geophys. Res. Lett.*, 30(23): 2194, doi. 10.1029/2003GL018477.

Levin, I. and B. Kromer, 2004. The tropospheric $^{14}CO_2$ level in mid-latitudes of the Northern Hemisphere (1959-2003). *Radiocarbon 46(3)*, 1261-1272.

Olivier, J.G.J. and J.J.M. Berdowski (2001) Global emissions sources and sinks. In: Berdowski, J., Guicherit, R. and B.J. Heij (eds.) "The Climate System", pp. 33-78. A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands. ISBN 90 5809 255 0.