



Radiocarbon in urban atmosphere: assessing fossil fuel CO₂ fluxes using combined measurements of CO₂, CO and ¹⁴CO₂/¹²CO₂ mixing ratios

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Emissions of carbon dioxide related to burning of fossil fuels (coal, oil and natural gas) constitute an important component of the carbon budget, both on global and regional scales. For heavily industrialized and populated areas such as western and central Europe, a large proportion of the total CO₂ flux entering the atmosphere is attributed to this source. Global and regional models of carbon cycle rely so far exclusively on emission statistics to quantify the magnitude and variability of the fossil CO₂ flux into the atmosphere. The combined measurements of CO and CO₂ mixing ratios on a given area, when calibrated using independent measurements of ¹⁴CO₂/¹²CO₂ ratios in atmospheric CO₂ may provide an independent way of assessing local and regional fossil CO₂ fluxes and their temporal variability (Levin et al., 2003; Levin and Karstens, 2006).

Krakow (50°04'N, 19°55'E, 220 m a.s.l.) is a large urban agglomeration located in the southern Poland, with about 1 million inhabitants, rapidly growing car traffic and significant industrial activities. Consumption of coal, gas and oil for communal and transport purposes generates major fluxes of anthropogenic carbon dioxide and carbon monoxide within the region. In addition, due to prevailing westerly air circulation, the Krakow region is under substantial influence of a large coal mining and industrial centre (Upper Silesia) located approximately 60 km west of the city.

The ¹⁴CO₂/¹²CO₂ ratios measured in Krakow since 1983 testify major changes in economy of the region which have occurred since 1989. The ¹⁴C signature of atmospheric CO₂ reflects significant changes in anthropogenic CO₂ fluxes released into the atmosphere both on local and regional scales. The contribution of fossil-fuel derived CO₂ in the total CO₂ load of the lower atmosphere in Krakow decreased from approx-

imately 21 ppm in 1989 to around 10-12 ppm in the last few years. This change is linked with major reduction in coal consumption in Poland, from ca. 160 Mt in 1985 to 84 Mt in 2004.

The measurements of CO concentrations in urban atmosphere can serve as a substitute for costly determinations of $^{14}\text{CO}_2/^{12}\text{CO}_2$ mixing ratios, provided that the ratio $\text{CO}/\text{CO}_2(\text{fossil})$ is determined for the given area and its variability is adequately characterized. The average value of $\text{CO}/\text{CO}_2(\text{fossil})$ ratio derived for the period April 2003 - April 2006 for Krakow region is equal 27.6 ± 4.2 ppb CO per ppm of fossil CO_2 . No distinct seasonal changes of this ratio were detected so far. Occasionally, very high (above 70 ppb/ppm) and very low (below 10 ppb/ppm) values of the $\text{CO}/\text{CO}_2(\text{fossil})$ ratio have been observed. The emission-based CO/CO_2 ratios reported for the period 1998-2005 for major industrial sources in the Krakow region are in the range between 7.3 and 10.8 ppb CO per ppm of fossil CO_2 . However, they do not comprise emissions related to car traffic which is an important source of fossil fuel CO_2 .

Also other trace substances of anthropogenic origin (PAHs, CHCl_3 , CH_3CCl_3 , CCl_4 , SF_6 , F11, F12, F113) have been tested as potential proxies of fossil fuel CO_2 emissions in the urban environment. The results of these trials are presented and discussed.

This work was supported by EU CARBOEUROPE integrated project and by the statutory funds of the AGH University of Science and Technology (project No.11.11.220.01).

References:

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