



Apportionment of carbon dioxide over central Europe: insights from combined measurements of atmospheric CO₂ mixing ratios and carbon isotope composition

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The European continent, due to high population density and numerous sources of anthropogenic CO₂ emissions, plays an important role in the global carbon budget. Nowadays, precise measurements of CO₂ mixing ratios performed by both global and regional monitoring networks, combined with appropriate models of carbon cycle, allow quantification of the European input to the global atmospheric CO₂ load. However, measurements of CO₂ mixing ratios alone cannot provide the information necessary for the apportionment of fossil-fuel related and biogenic contributions to the total CO₂ burden of the regional atmosphere. Additional information is required, for instance obtained through measurements of radiocarbon content in atmospheric carbon dioxide. Radiocarbon is a particularly useful tracer for detecting fossil carbon in the atmosphere on different spatial and temporal scales.

Regular observations of atmospheric CO₂ mixing ratios and their isotope compositions have been performed during the period of 2005-2009 at two sites located in central Europe (southern Poland). The sites, only ca. 100 km apart, represent two extreme environments with respect to the extent of anthropogenic pressure: (i) the city of Krakow, representing typical urban environment with numerous sources of anthropogenic CO₂, and (ii) remote mountain site Kasprowy Wierch, relatively free of local influences. Regular, quasi-continuous measurements of CO₂ mixing ratios have been performed at both sites. In addition, cumulative samples of atmospheric CO₂ have been collected (weekly sampling regime for Krakow and monthly for Kasprowy Wierch) to obtain mean carbon isotope signature (¹⁴C/¹²C and ¹³C/¹²C ratios) of atmospheric CO₂ at both sampling locations. Partitioning of the local atmospheric CO₂ load at both locations has been performed using isotope- and mass balance approach.

In Krakow, the average fossil-fuel related contribution to the local atmospheric CO₂ load was equal to approximately 3.4%. The biogenic component turned out to be of the same magnitude. Both components revealed a distinct seasonality, with the fossil-fuel related component reaching maximum values during winter months and the biogenic component shifted in phase by ca. 6 months. Seasonality of fossil-fuel related CO₂ load in the local atmosphere is linked with seasonality of local CO₂ sources, mostly burning of fossil fuels for heating purposes. Positive values of biogenic component indicate prevalence of the local respiration and biomass burning processes over local photosynthesis. Summer maxima of biogenic CO₂ component represent mostly local respiration activity. Direct measurements of soil CO₂ fluxes in the Krakow region showed an approximately 10-fold increase of those fluxes during the summer months.

Partitioning of the local CO₂ budget for Kasprowy Wierch site revealed large differences in the derived components when compared to urban atmosphere of Krakow: the fossil-fuel related component was ca. 5 times lower whereas the biogenic component was negative in summer, pointing to the importance of photosynthetic sink associated with extensive forests in the neighborhood of the station.

The isotope- and mass balance approach was also used to derive mean monthly ¹³C isotope signature of fossil-fuel related CO₂ emissions in Krakow. Although the derived $\delta^{13}\text{CO}_2$ values revealed large variability, they are confined in the range of ¹³C isotope composition being reported for various sources of CO₂ emissions in the city (burning of coal and oil, burning of methane gas, traffic).