



Carbon-13 isotope composition of the mean CO₂ source in the urban atmosphere of Krakow, southern Poland

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Quantification of carbon emissions in urbanized areas constitutes an important part of the current research on the global carbon cycle. As the carbon isotopic composition of atmospheric carbon dioxide can serve as a fingerprint of its origin, systematic observations of $\delta^{13}\text{CO}_2$ and/or $\Delta^{14}\text{CO}_2$, combined with atmospheric CO₂ mixing ratio measurements can be used to better constrain the urban sources of this gas. Nowadays, high precision optical analysers based on absorption of laser radiation in the cavity allow a real-time monitoring of atmospheric CO₂ concentration and its $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio, thus enabling better quantification of the contribution of different anthropogenic and natural sources of this gas to the local atmospheric CO₂ load.

Here we present results of a 2-year study aimed at quantifying carbon isotopic signature of the mean CO₂ source and its seasonal variability in the urban atmosphere of Krakow, southern Poland. The Picarro G2101-i CRDS isotopic analyser system for CO₂ and $^{13}\text{CO}_2/^{12}\text{CO}_2$ mixing ratio measurements has been installed at the AGH University of Science and Technology campus in July 2011. Air inlet was located at the top of a 20m tower mounted on the roof of the faculty building (ca. 42m a.g.l.), close to the city centre. While temporal resolution of the analyser is equal 1s, a 2-minute moving average was used for calculations of $\delta^{13}\text{CO}_2$ and CO₂ mixing ratio to reduce measurement uncertainty. The measurements were calibrated against 2 NOAA (National Oceanic and Atmospheric Administration) primary standard tanks for CO₂ mixing ratio and 1 JRAC (Jena Reference Air Cylinder) isotope primary standard for $\delta^{13}\text{C}$. A Keeling approach based on two-component mass and isotope balance was used to derive daily mean isotopic signatures of local CO₂ from individual measurements of $\delta^{13}\text{CO}_2$ and CO₂ mixing ratios. The record covers a 2-year period, from July 2011 to July 2013. It shows a clear seasonal pattern, with less negative and less variable $\delta^{13}\text{CO}_2$ values during the late spring, summer and early autumn, and more negative and more noisy $\delta^{13}\text{CO}_2$ values during the rest of the year. The mean $\delta^{13}\text{CO}_2$ value for summer months (May–September) is equal $-29.44 \pm 0.12\text{‰}$ while during winter it drops to $-33.29 \pm 0.28\text{‰}$. The isotopic signature of mean summer CO₂ source represents strong biogenic CO₂ emissions ($\delta^{13}\text{CO}_2 \cong -28\text{‰}$) mixed with isotopically similar CO₂ emitted by car traffic in the city ($\delta^{13}\text{CO}_2 \cong -30\text{‰}$). During the cold period, biogenic source becomes negligible, while anthropogenic CO₂ emissions are enhanced by heating of the households. The CO₂ sources associated with heating represent a much wider range of isotope composition (from -24‰ for coal burning, -28‰ for burning of wood in fireplaces, down to -54‰ for heating systems supplied with natural gas of Siberian origin).

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