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Seasonal variability of soil CO2 flux and its stable isotope composition in an urban area: case study from Krakow, southern Poland

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Attempts to quantify the role of urban areas in the global carbon budget have been so far focused mainly on quantifying anthropogenic emissions of carbon dioxide. On the other hand, numerous studies have been performed focusing on biogenic CO_2 emissions, including characterization of soil CO_2 fluxes for different ecosystems (grassland, cropland, forest etc.). Stable isotope composition of CO_2 carries additional information with respect to the origin of this trace gas. Several studies focusing on the isotope mass balance as a tool to identify the contribution of different CO_2 sources to the atmospheric load of this gas, have been published in the literature.

The presented work is an attempt to assess the impact of urban areas on atmospheric levels of CO_2 and to characterize stable isotope signature of biogenic CO_2on the areas with different anthropogenic influence. The soil CO_2 efflux and its carbon and oxygen isotopic signature was measured on the monthly basis in the period from July 2009 to June 2010. The measurements were performed at four locations within the metropolitan area of Krakow, representing different level of anthropogenic influence. The site with heaviest impact was located in direct neighborhood of a busy street. Two other sites representing medium anthropogenic influence were placed within green recreation area. The last site one was located at the outskirts of the city, at the distance of ca. 12 km from the city center. The soil CO_2 efflux was measured using a closed chamber system coupled with Vaisala CARBOCAP sensor. The isotopic signature of the respiration CO_2 was determined with the aid of two air samples collected to 1-liter glass flasks, one at the beginning, and one at the end of the measurement cycle. Two component mixing model was applied to calculate isotopic signature of the source.

The measurements show that magnitude of soil CO_2 efflux is a subject of strong seasonal variation, which is a consequence of natural biospheric activity cycle. Maximum values of the CO_2 efflux were measured during summer (up to 43.7$\pm$3.1 mmol $m^{-2}h^{-1}$ recorded in September 2009). The minima were observed during winter, with the values fluctuating between 1 and 3 mmol $m^{-2}h^{-1}$. The differences between the measurement sites reached in summer ca. 23 mmol $m^{-2}h^{-1}$. They were not correlated with the presumed degree of anthropogenic influence at different sites. During winter the differences between sites were negligible.

The carbon isotopic signature of soil CO_2 ($\delta^{13}C$) fluctuated at three sites between -26 and -30‰ as expressed on the V-PDB scale. Such values of $\delta^{13}C$ indicate a domination of C3-type vegetation cover existing there. At one site of medium anthropogenic influence, located inside the university campus close to the city center, the carbon isotope signature of soil CO_2efflux was less negative (-21.6$\pm$0.2‰) pointing to larger contribution of C4-type vegetation in this area. Apparently, carbon isotopic composition of soil CO_2 efflux at the investigated sites did not revealed any significant influence of fossil-fuel CO_2 present in urban environment and taken up by plants living there.

Large seasonal variability of oxygen isotopic composition of soil CO_2 efflux was observed. During summer, $\delta^{18}O$ values of soil CO_2 efflux (expressed on the VPDB-CO_2 scale) were fluctuating around 0‰ at all measurement sites, while during winter very negative $\delta^{18}O$ values were observed. Extreme value of -34.5$\pm$0.6‰ was recorded in February 2010. While the carbon isotope composition of soil CO_2 efflux is primarily controlled by isotopic signature of the respired CO_2 (both autotrophic and heterotrophic component), its oxygen isotope composition is controlled in the first instance by isotopic composition of the soil moisture which varies in accordance with $\delta^{18}O$ values in precipitation. Another important parameter is the temperature at which the isotope exchange between soil CO_2 and soil moisture takes place.

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