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Seasonal and diurnal variations of greenhouse gases in Florence (Italy): inferring sources and sinks from carbon isotopic ratios

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By 2050, more than two-thirds of global population is expected to live in urban areas. In order to guarantee a sustainable development and the achievement of the greenhouse gas (GHG) emissions reduction set by the Paris Agreement, city administrators must adopt urban planning strategies and local policy initiatives aimed to lowering the urban carbon footprint. The Municipality of Florence (Italy) has recently renewed its intent to cut urban CO_2 emissions of 50 % by 2030 through a series of actions aimed to decrease GHGs contributions from vehicular traffic by amending citizens attitudes towards urban mobility. Nevertheless, Florence is still affected by poor air quality conditions.

The effectiveness of intervention plans depends on the availability of a clear and complete knowledge of the emitting sources and their relative contributions to urban air quality and has to be verified with monitoring surveys of GHGs emissions and concentrations. This study presents the results of a continuous monitoring (from 7 to 21 July, 2017 and from October 10 to December 15, 2017) of (i) CO_2 fluxes, and (ii) atmospheric CO_2 and CH_4 concentrations and carbon isotopic ratios ($\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4) from a monitoring site located in the city centre.

CO_2 flux data revealed that the metropolitan area acted as a net source of CO_2 during the whole observation period. The separation of the different anthropogenic contributions to atmospheric CO_2, investigated on the basis of the Keeling plot analysis, revealed gasoline combustion contributing for about 30 % and natural gas combustion for about 70 %, with the latter contributing 7 times more in December than in July. The measured CO_2 fluxes were about 80 % larger in autumn than in summer, further confirming that domestic heating based on natural gas is the dominant CO_2 emitting source in Florence. The current urban green infrastructures are not sufficient to counterbalance the emissions from anthropogenic sources, even during the plants vegetative season. Nevertheless, the continuous monitoring revealed a $\delta^{13}C$-CO_2 shift in October, during the central hours of the day, towards values lower than those expected for simple mixing between background and anthropogenic CO_2, suggesting that photosynthetic withdrawal of atmospheric CO_2 might partially contribute to reduce CO_2 concentrations at peculiar periods prior to the heating season.

During autumn, atmospheric CH_4 concentrations sensibly increased with respect to summer levels, whilst $\delta^{13}C$-CH_4 shifted towards heavier values. The diurnal isotopic ratios of CH_4 in July were relatively constant, pointing to the absence of relevant local emitting sources during daytime, and oscillated around -51 ‰ vs. V-PDB, i.e. a value typical of biogenic sources. During fall, monthly average $\delta^{13}C$-CH_4 values around -45 ‰ vs. V-PDB confirmed the overwhelming contribution from natural gas, likely related to CH_4 leaks from the city distribution network. However, in October, a peak towards heavier $\delta^{13}C$-CH_4 values was observed in working days during the afternoon rush hour (around 17:00), suggesting that also vehicular exhaust emissions partially contribute to atmospheric CH_4.