Diurnal and seasonal changes of $\delta^{13}C$ and $\delta^{18}O$ in carbon dioxide measured by eddy covariance over an urban surface

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The isotopic composition of the greenhouse gas CO_2 can provide valuable information about its sources. For example, linear mixing models have been used to identify the sources of enhanced CO_2 in the urban atmosphere using urban and background measurements of atmospheric mixing ratios in combination with known source signatures [1,2]. Here we propose and test an alternative approach by continuously and directly measuring isofluxes of urban emissions. We directly measure the fluxes of the stable isotopes $^{12}CO_2$, $^{13}CO_2$ and $CO^{18}O$ by means of eddy covariance (EC) on an urban flux tower.

Goals

- ❶ **Determine directly the characteristic isotopic composition** of the urban emission mix of a typical urban surface using EC.
- ❷ **Determine changes in the isoflux ratios** over time with changing strength of fuel and respiratory emissions (from soils, plants, and humans).
- ❸ **Compare measured isoflux ratios to emission inventories** using known source signatures.

Methods

EC isofluxes were continuously measured on UBC's flux tower located in Vancouver, BC, Canada (Fluxnet ID "Ca-VSu") between March 15 and June 30, 2016. The tower is located near a major intersection of two arterial roads (70,000 vehicles day^{-1}) in a residential area that also exhibits building emissions from natural gas use.

EC-isofluxes were measured with a sonic anemometer (CSAT-3, Campbell Scientific Inc.) installed at 28 m above the ground and a co-located inlet for air sampling.

Air was drawn through a tube to a climate-controlled trailer at the base of the tower, where a **closed-path tuneable diode laser absorption spectroscopy** (TDLAS) system scanned absorption lines at 2308.171 cm^{-1} ($^{13}CO_2$), 2308.225 cm^{-1} ($^{12}CO_2$) and 2308.416 cm^{-1} ($CO^{18}O$) at 10 Hz (TGA200, Campbell Scientific Inc.). Every 10 minutes, the TDLAS was calibrated using three tanks referenced against NOAA-ESRL/INSTAAR, UoC standards.

Half-hourly isoflux ratios were calculated as

$$F^{13}C = 1000\left(\frac{\overline{w'\,^{13}CO_2'}/\overline{w'\,^{12}CO_2'}}{R_{PDB-CO_2}} - 1\right)$$

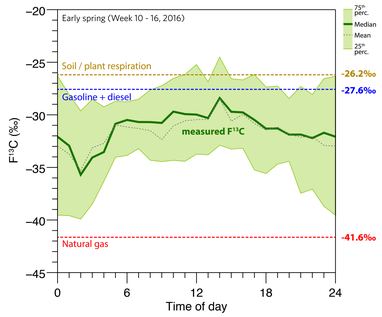
and

$$F^{18}O = 1000\left(\frac{\overline{w'\,CO^{18}O'}/\overline{w'\,^{12}CO_2'}}{R_{PDB-CO_2}} - 1\right)$$

Unlike $\delta^{13}C_s$ determined via the intercept of 'Keeling plots' [3], isoflux ratios $F^{13}C$ and $F^{18}O$ directly characterize the source composition of the CO_2 flux, without the need for background measurements. Consequently, isoflux ratios change instantaneously with the flux and are linked to the local tower source area, while the 'Keeling plot' approach is based on mixing ratios that are the result of accumulated and transported CO_2 over hours/days in the boundary layer.

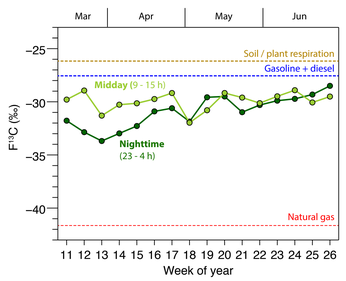
Results for $F^{13}C$

From independent source sample analysis in Vancouver [4], we know that $\delta^{13}C$ in CO_2 primarily separates between CO_2 emitted from natural gas (-41.5‰ ±0.93) versus gasoline (-27.3‰ ±0.40) and diesel (-28.8‰ ±0.82). The signature of typical respiration, with -26.2‰ [3], is close, however.



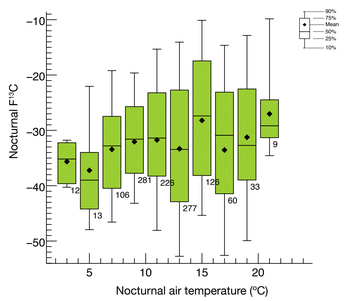
Diurnal course in $F^{13}C$. In spring, $F^{13}C$ changed over the course of a day, with lowest (most negative) values in the early morning, and highest values midday. During night, a higher fraction of natural gas emissions is expected, while daytime emissions are dominated by gasoline and diesel (traffic). This explanation assumes respiratory fluxes were minor and steady at that time of the year.

Seasonal trends in $F^{13}C$. During the transition from spring to summer, overall $F^{13}C$ increased. Most notably the difference between nighttime and daytime $F^{13}C$ was progressively reduced. In early spring, home heating by natural gas was a major source of CO_2. In early summer a larger fraction of nighttime emissions was likely from soil respiration.



The average $F^{13}C$ matches well with estimates from a top-down fuel inventory for the entire City of Vancouver. A city-wide fuel inventory separates emission into 36% natural gas (N) and 64% gasoline and diesel (G+D) for the period March to June, which would lead to a calculated average $F^{13}C$ = -32.7‰ (as opposed to the measured -32.1‰). Over the four months, EC-measured $F^{13}C$ increased from a low of -33.1‰ in March to high of -31.7‰ in June, which is explained by a proportional decrease of emissions from home heating (natural gas), a trend which is also reflected in the model (which is based on a typical meteorological year for heating).

Month	Measured $F^{13}C$ (‰)	Modelled $F^{13}C$ (‰)	Measured ratio N : (G+D)	Modelled ratio N : (G+D)
March	-33.1	-34.4	39% : 61%	48% : 52%
April	-31.8	-33.3	30% : 70%	41% : 59%
May	-31.8	-32.0	30% : 70%	31% : 69%
June	-31.7	-31.0	29% : 71%	34% : 76%
Mar-Jun	**-32.1**	**-32.7**	**32% : 68%**	**36% : 64%**

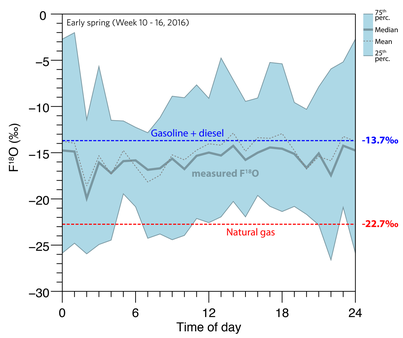


Nocturnal (23-04h) $F^{13}C$ is positively correlated with air temperature, underlining both, the role of increased natural gas emissions and decreased soil respiration rates in cool early spring nights, and reduced natural gas emissions and higher soil respiration in early summer nights.

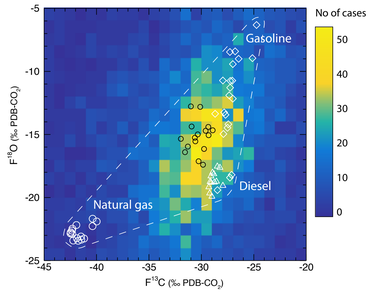
Results for $F^{18}O$

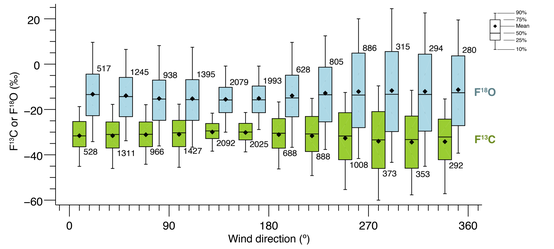
$\delta^{18}O$ in CO_2 from vehicle emissions is fractionated in catalytic converters ($\delta^{18}O$ with converter: -12.5‰; no converter -18.6‰; natural gas -22.7‰, the latter is close to atmospheric oxygen [4]). $\delta^{18}O$ in CO_2 from biogenic emissions exhibit a larger seasonal variability due to changes in plant water origin and fractionation during the dry season.

Diurnal course in $F^{18}O$. $F^{18}O$ changed less over the course of a day, yet lowest values were again found in the early morning, likely due to the dominance of nocturnal natural gas emissions (home heating) as opposed to gasoline and diesel during the day (traffic dominated).



$F^{13}C$ and $F^{18}O$ are positively correlated, and generally fall within the expected range of fuel source end-members. The white symbols show independent samples taken from exhaust of various fuel sources in Metro Vancouver [4]. The dashed line encircles the expected range of $F^{18}O$ and $F^{13}C$ if only fuels are considered. Black circles are weekly averages of $F^{18}O$ and $F^{13}C$.





$F^{13}C$ and $F^{18}O$ also showed a directional dependence with changing turbulent source areas. Highest $F^{18}O$ and lowest $F^{13}C$ were measured when wind was from the NW to the tower - a source area characterized by significant tree cover, homes and lack of major roads. In contrast, when wind came from the SE, where the busy intersection is located, $F^{18}O$ showed lowest values and $F^{13}C$ highest. Note that these directional relations are in contrast to the statistical relationship above.

Conclusions and applications

Over four months, we measured continuously and successfully isofluxes of CO_2 by eddy covariance (EC) over an urban surface. We show that EC-measured isofluxes result in $F^{13}C$ and $F^{18}O$ values that are consistent with independent source samples and a municipal inventory. This approach could be useful to partition long-term EC fluxes of CO_2 on urban EC-towers and hence add additional information to validate fine-scale emission inventories, and/or to provide valuable information about the characteristic (and changing) isotopic composition of urban emission mixes for cities for use in regional and global inversion models.

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