Using stable carbon and oxygen isotopes to attribute measured carbon-dioxide emissions in urban environments to different fuel sources.

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Motivation

The recent decade has seen a rapid adoption and advancement of methods to interpret direct measurements of carbon dioxide ($CO_2$) in urban environments to provide independent carbon emission estimates at urban scales.

Although several studies demonstrate potential of using direct measurements to validate fine-scale emission inventories of $CO_2$, a major challenge remains the source attribution of total measured mass fluxes or concentrations of $CO_2$ to various sources.
The challenge of source attribution

Measured net mass flux of carbon dioxide

\[ F_{CO_2} = C + R - P + \Delta S \]

A partitioning of \( F_{CO_2} \) into the different fuel and biogenic sources is not possible using current approaches.
Research question

Can stable isotope composition of CO$_2$ add additional information on fuel sources and hence complement emission and concentration measurements of CO$_2$ in urban environments?

The 3 most abundant isotopologues of CO$_2$ in the atmosphere are:

- $^{13}$C$^{16}$O$_2$ ~1.10% ~4 ppm
- $^{12}$C$^{16}$O$_2$ ~98.43% ~400 ppm
- $^{12}$C$^{16}$O$^{18}$O ~0.39% ~1.5 ppm

$\delta^{13}$C $\delta^{18}$O
Stable isotope ratios

We express the relative abundance (ratios) of the different isotopologues in delta-notation:

\[
\delta^{13}C = 1000 \cdot \left( \frac{\left[ ^{13}C^{16}O_2 \right]}{\left[ ^{12}C^{16}O_2 \right]} \cdot \frac{R_{VPDB}}{1} \right)
\]

\[
\uparrow \text{Ratio of a pre-defined standard sample}
\]

\[
\delta^{18}O = 1000 \cdot \left( \frac{\left[ ^{12}C^{16}O^{18}O \right]}{\left[ ^{12}C^{16}O_2 \right]} \cdot \frac{R_{SMOW}}{1} \right)
\]

\[
\uparrow \text{Ratio of a pre-defined standard sample}
\]
We can measure CO$_2$-isotopologues directly in-situ in the urban atmosphere using a spectroscopy system (here: TGA 200, Campbell Scientific Inc., Logan UT).
Laser spectroscopy of CO$_2$ isotopologues

At low pressure, absorption bands separate
Objectives

1. Determine the typical $\delta^{13}C$ and $\delta^{18}O$ of various emission sources contributing to CO$_2$ in the urban boundary layer over Vancouver, Canada.

2. Determine the CO$_2$ enhancement in Vancouver’s urban boundary layer.

3. Measure the $\delta^{13}C$ and $\delta^{18}O$ of the enhancement directly and determine whether the added (i.e. enhanced) CO$_2$ reflects the isotopic signatures of the typical CO$_2$ sources expected.
Major fuel sources separate well!

- Gasoline
- Diesel
- Natural gas

$\delta^{13}\text{C} ($‰ VPDB-CO$_2$)

$\delta^{18}\text{O} ($‰ VPDB-CO$_2$)

Exhaust samples
TEDLAR bags
Dilution and analysis in lab
However soil and plant respiration overlap with gasoline.
Downtown

Year-round measurements on UBC campus

3m, urban background, 200m from nearest road
Urban CO₂ enhancement

Winter (Dec–Feb)

CO₂ Mixing Ratio (ppm)

<table>
<thead>
<tr>
<th>Time of day (LST)</th>
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Vancouver (Urban) 423.4 ppm

Estevan Point (Pristine) 403.0 ppm

Spring (Mar–May)

CO₂ Mixing Ratio (ppm)

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Vancouver (Urban) 414.9 ppm

Estevan Point (Pristine) 403.3 ppm

Summer (Jun–Aug)

CO₂ Mixing Ratio (ppm)

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Vancouver (Urban) 415.2 ppm

Estevan Point (Pristine) 396.2 ppm

Fall (Sep–Nov)

CO₂ Mixing Ratio (ppm)

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Vancouver (Urban) 419.0 ppm

Estevan Point (Pristine) 404.6 ppm

Annual average difference: 418.2 ppm - 401.8 ppm = 16.4 ppm
Mixing ratio

Isotope ratio for $^{13}$C

Tropospheric Background
397.34 ppm

Hour of day (PST)
0 6 12 18 24

Mixing ratio

Tropospheric background

Vancouver UBC
27-04-13 to 07-05-13
‘Keeling plot’ for a 24 hour period

\[ \delta^{13}C \text{ (per mil)} \]

\[ 1/\left[ \text{CO}_2 \right] \text{ (ppm}^{-1}) \]

Winter
January 19, 2013

\(-31.83 \text{ \%o}\)
‘Keeling plots’ for a day in winter and spring

\[ \delta^{13}C \text{ (per mil)} = -29.05 \% \]

Winter
January 19, 2013

\[ \delta^{13}C \text{ (per mil)} = -31.83 \% \]

Spring
May 5, 2013
Community Energy and Emissions Inventory

5.26 Mt CO$_2$e yr$^{-1}$

- **45.8% Gasoline**
- **41.7% Natural gas**
- **11.5% Diesel**

Vehicles

Buildings

kt CO$_2$e month$^{-1}$

- Jan
- Feb
- Mar
- Apr
- May
- Jun
- Jul
- Aug
- Sep
- Oct
- Nov
- Dec
Comparing CEEI and Isotopes

**Observation**
Based on $\delta^{13}C$ of CO$_2$ in urban atmosphere

- January:
  - Natural gas: 53%
  - Gasoline: 47%

- May:
  - Natural gas: 25%
  - Gasoline: 75%

**Inventory**
Monthly distributed CEEI / BEM for entire metropolitan area

- January:
  - Natural gas: 58%
  - Gasoline: 42%

- May:
  - Natural gas: 31%
  - Gasoline: 69%
Intercepts change over year

In winter, when there is home heating (natural gas), there is lower $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from city sector
Intercepts are temperature dependent

Colder temperatures mean more heating using natural gas (lower $\delta^{13}C$)
Intercepts change over day and year

\[ \delta^{13}C = -26.7^{\circ}\text{‰} \]

\[ \delta^{18}O = -16.9^{\circ}\text{‰} \]

\[ \delta^{13}C = -30.9^{\circ}\text{‰} \]

\[ \delta^{18}O = -22.9^{\circ}\text{‰} \]

\[ \delta^{13}C = -32.2^{\circ}\text{‰} \]

\[ \delta^{18}O = -29.0^{\circ}\text{‰} \]

\[ \delta^{13}C = -32.1^{\circ}\text{‰} \]

\[ \delta^{18}O = -11.6^{\circ}\text{‰} \]

\[ \delta^{13}C = -28.6^{\circ}\text{‰} \]

\[ \delta^{18}O = -10.0^{\circ}\text{‰} \]

\[ \delta^{13}C = -9.6^{\circ}\text{‰} \]

\[ \delta^{18}O = -16.9^{\circ}\text{‰} \]

\[ \delta^{13}C = -26.7^{\circ}\text{‰} \]

\[ \delta^{18}O = -10.0^{\circ}\text{‰} \]

\[ \delta^{13}C = -29.0^{\circ}\text{‰} \]

\[ \delta^{18}O = -9.6^{\circ}\text{‰} \]

\[ \delta^{13}C = -32.1^{\circ}\text{‰} \]
Annual changes in isotopic signatures

\[ \delta^{18}O \text{ (‰ VPDB-CO}_2) \]

\[ \delta^{13}C \text{ (‰ VPDB-CO}_2) \]

Unusually cold

Gasoline

Diesel

Natural gas
The urban boundary layer (UBL) of Vancouver is enriched by CO$_2$ by on average +15 ppm.

Natural gas separates well from all other sources with its low $\delta^{13}$C (-41.6‰) and low $\delta^{18}$O (-22.7‰).

Atmospheric measurements of $\delta^{13}$C confirm that the UBL contains a higher fraction of CO$_2$ from natural gas in winter and night, and more gasoline / diesel during summer and day, consistent with inventories.

Challenges: The $\delta^{13}$C of gasoline (-27.3‰) is close to diesel (-28.8‰) and overlaps with respiration. $\delta^{18}$O has large variations.

Continuous measurements of isotopic composition have potential to complement emission estimates at urban scales.
Challenges and next steps

• Understand more carefully **what controls δ\(^{18}\)O variations** in gasoline exhaust and respiration and how they vary over the year.

• Explore a **3-end-member mixing model** using δ\(^{13}\)C and δ\(^{18}\)O on seasonal and diurnal scales.

• More carefully characterize **regional background**.

• Future: Develop eddy covariance measurements of CO\(_2\) isotopologues to characterize fleet signatures etc.