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

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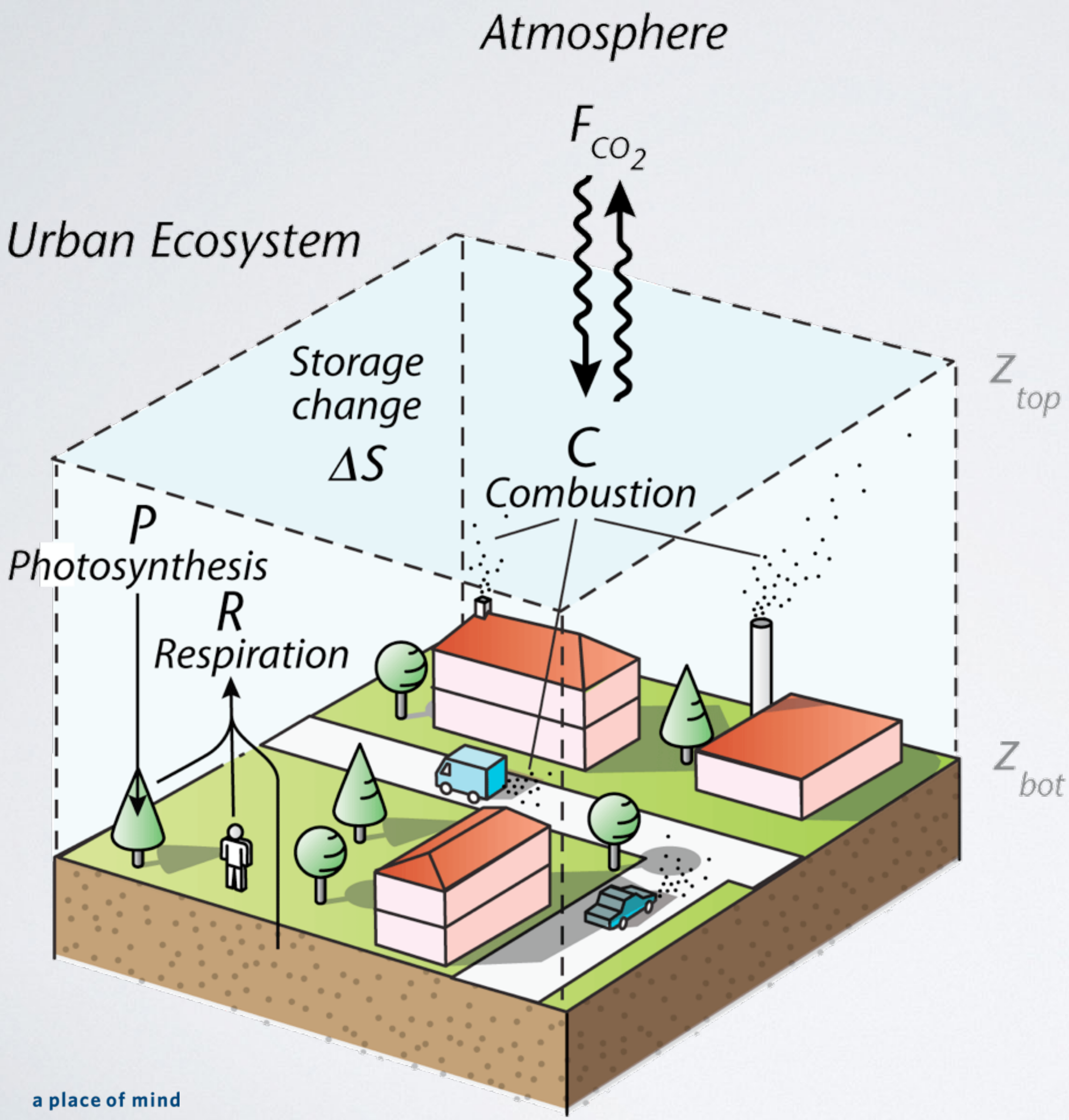
Vancouver (Photo: A. Christen)

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

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

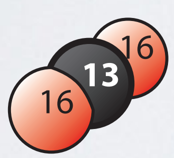
A partitioning of F_{CO2} into the different fuel and biogenic sources is not possible using current approaches.

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?

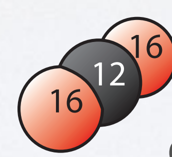
The 3 most abundant isotopologues of CO_2 in the atmosphere are:

$^{13}C^{16}O_2$



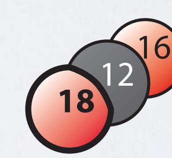
~1.10%
~4 ppm

$^{12}C^{16}O_2$



~98.43%
~400 ppm

$^{12}C^{16}O^{18}O$



~0.39%
~1.5 ppm

$\delta^{13}C$

$\delta^{18}O$

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Stable isotope ratios

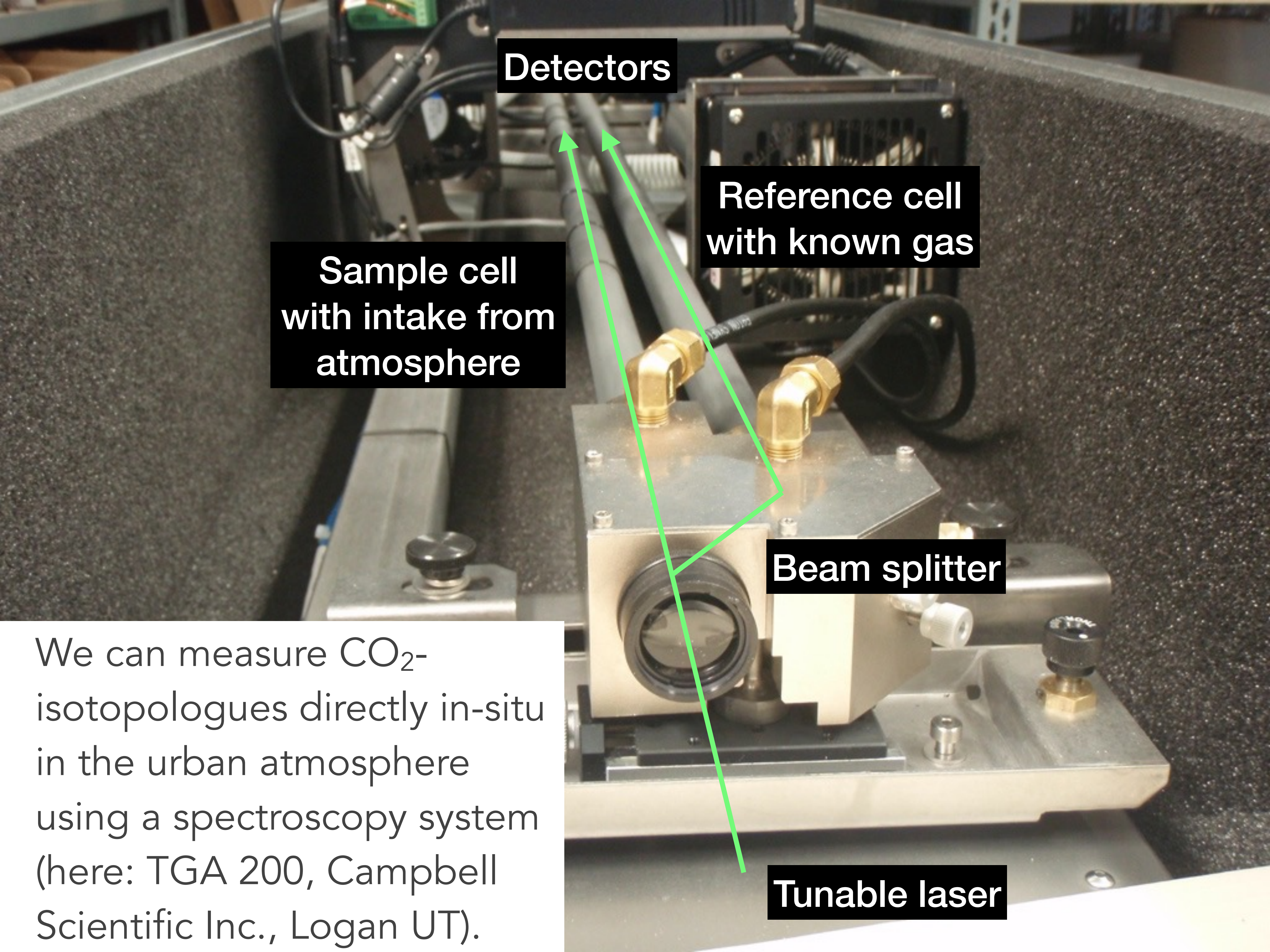
We express the relative abundance (ratios) of the different isotopologues in delta-notation:

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

↑ Ratio of a pre-defined standard sample

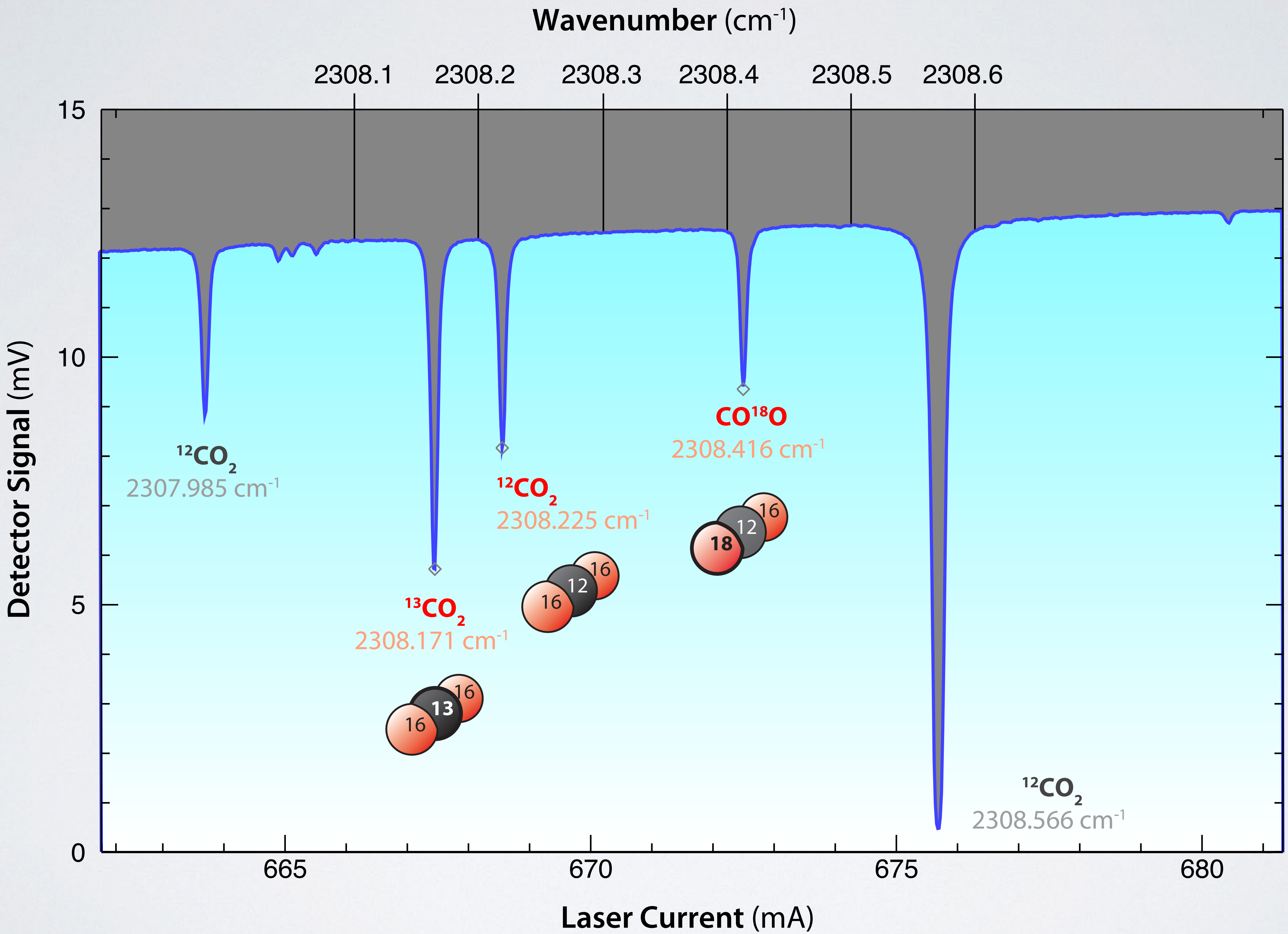
$$\delta^{18}O = 1000 \cdot \left(\frac{[^{12}C^{16}O^{18}O]/[^{12}C^{16}O_2]}{R_{SMOW}} - 1 \right)$$

↑ 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

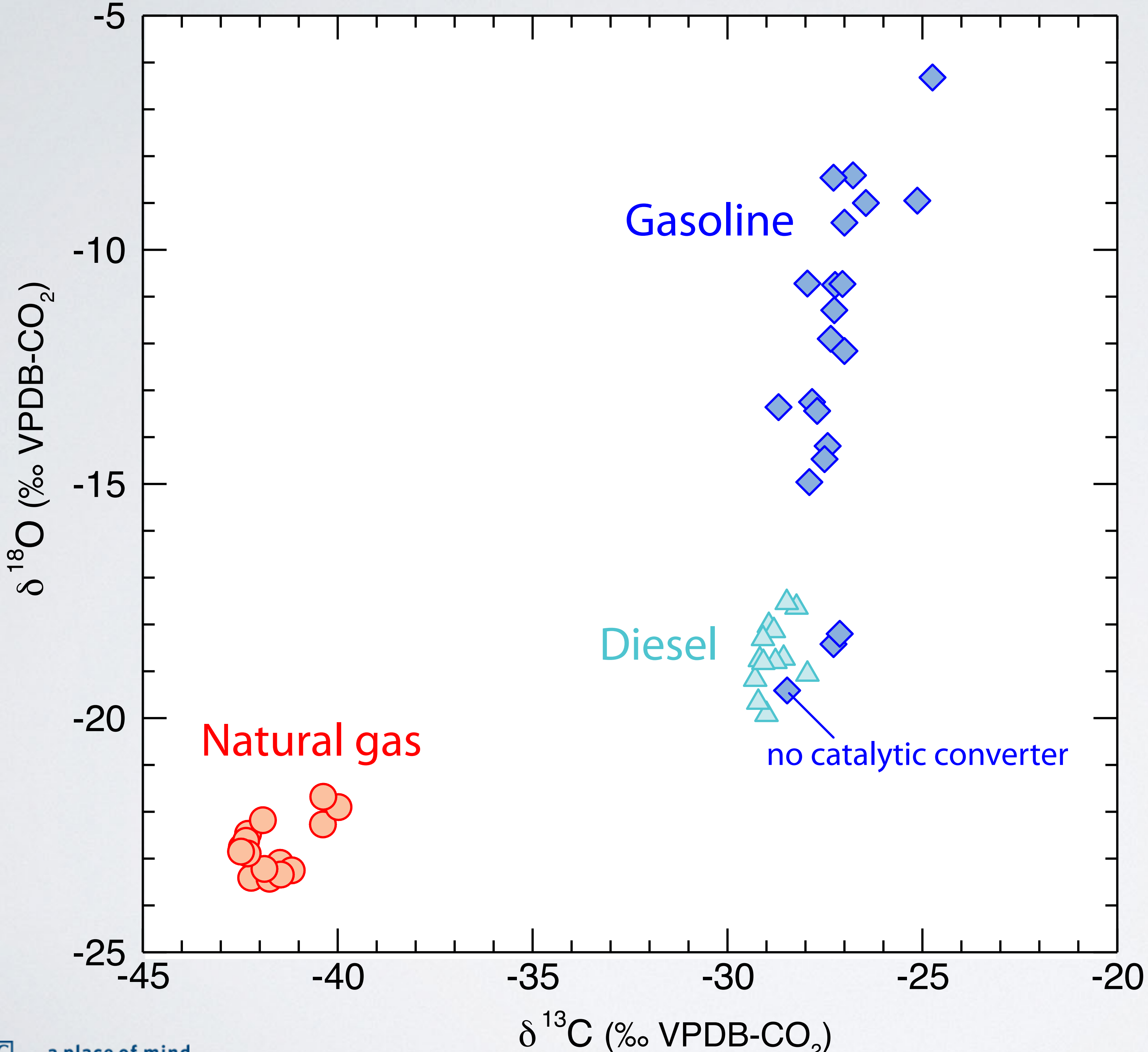
Objectives

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.

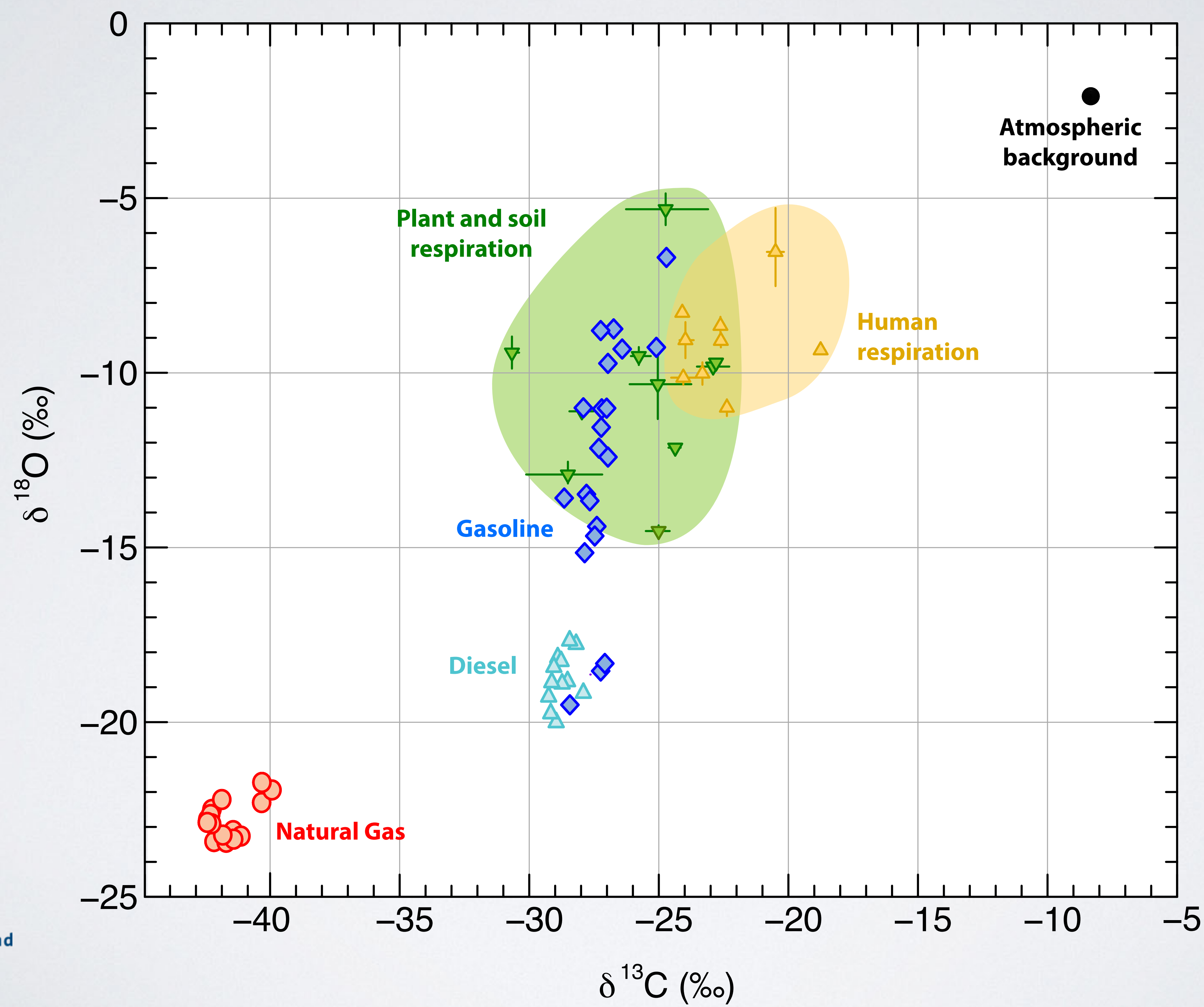
Major fuel sources separate well!



Exhaust samples

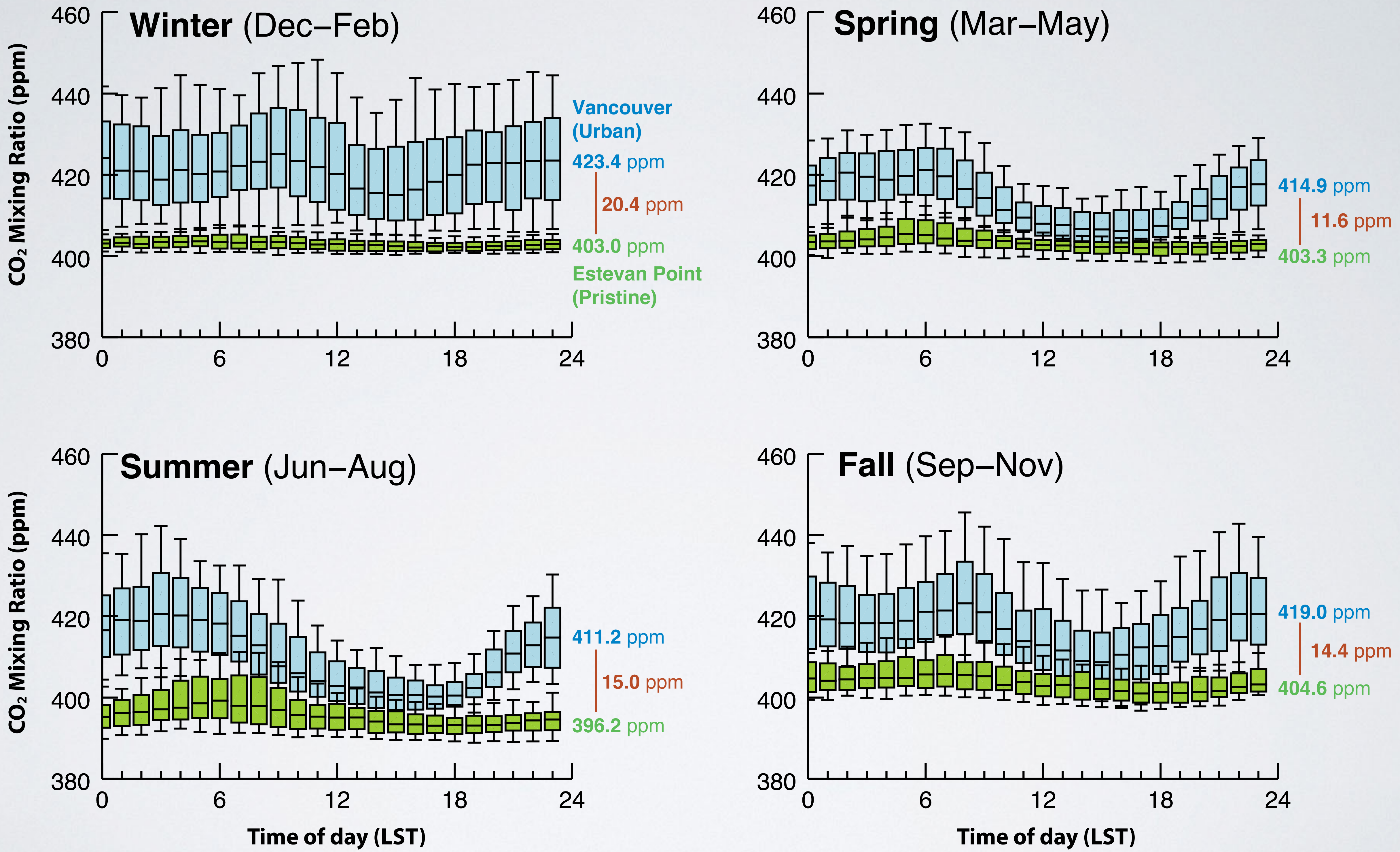
Dilution and analysis in lab

However soil and plant respiration overlap with gasoline




Urban
(Vancouver)
Canada
USA
240 km
Pristine
(Estevan Point)
50°N
Year-round
measurements
on UBC campus
Downtown
Ocean
3m, urban background, 200m from nearest road
Metro Vancouver (Photo: A. Christen)

Urban CO_2 enhancement



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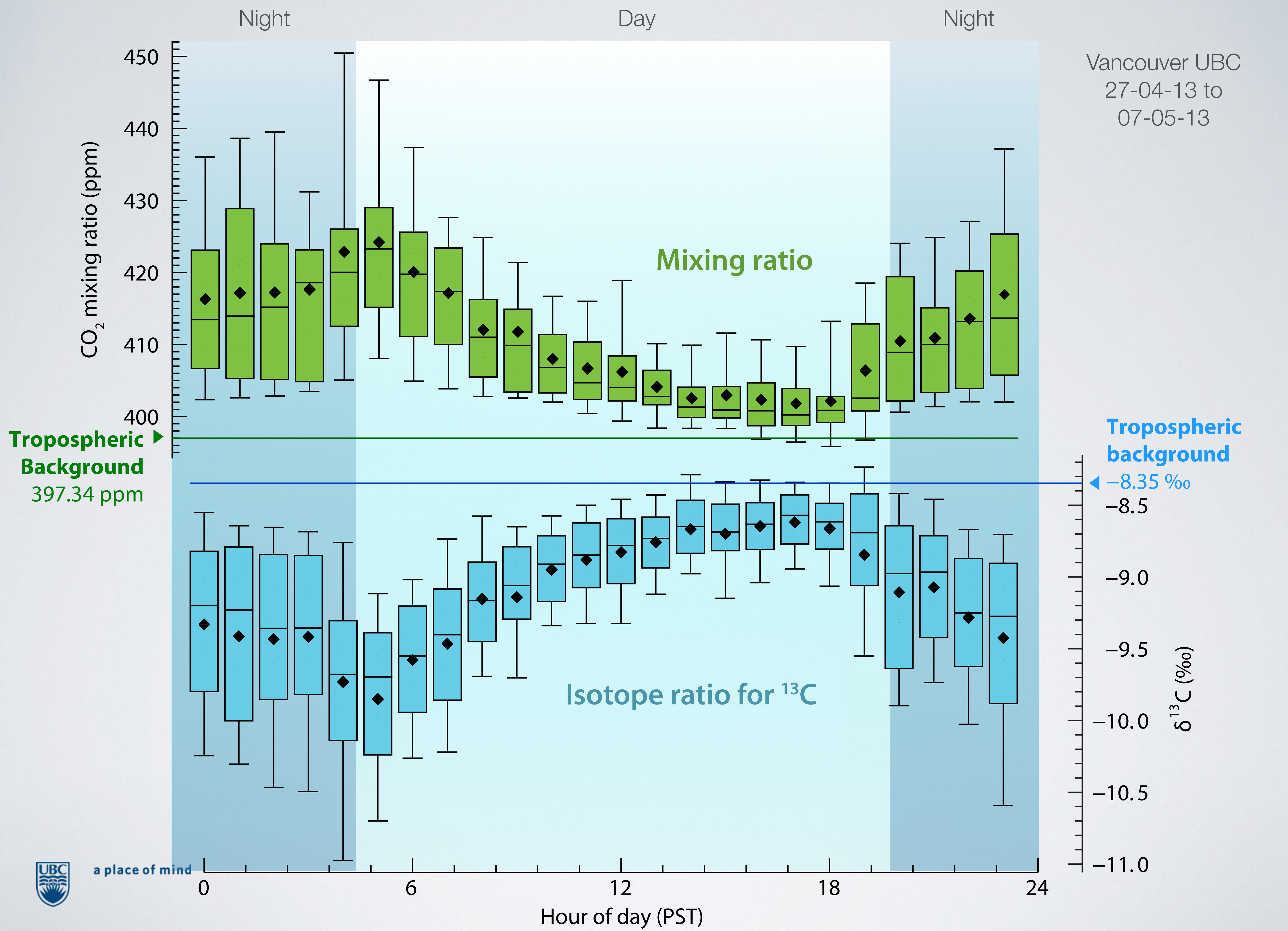
Annual average difference: 418.2 ppm - 401.8 ppm = 16.4 ppm



Night
Day
Night
Vancouver UBC
27-04-13 to
07-05-13
Mixing ratio
Isotope ratio for ^{13}C
CO_2 mixing ratio (ppm)
450
440
430
420
410
400
Tropospheric
Background
397.34 ppm
Tropospheric
background
−8.35 ‰
−8.5
−9.0
−9.5
−10.0
−10.5
−11.0
$\delta^{13}C$ (‰)
0
6
12
18
24
Hour of day (PST)
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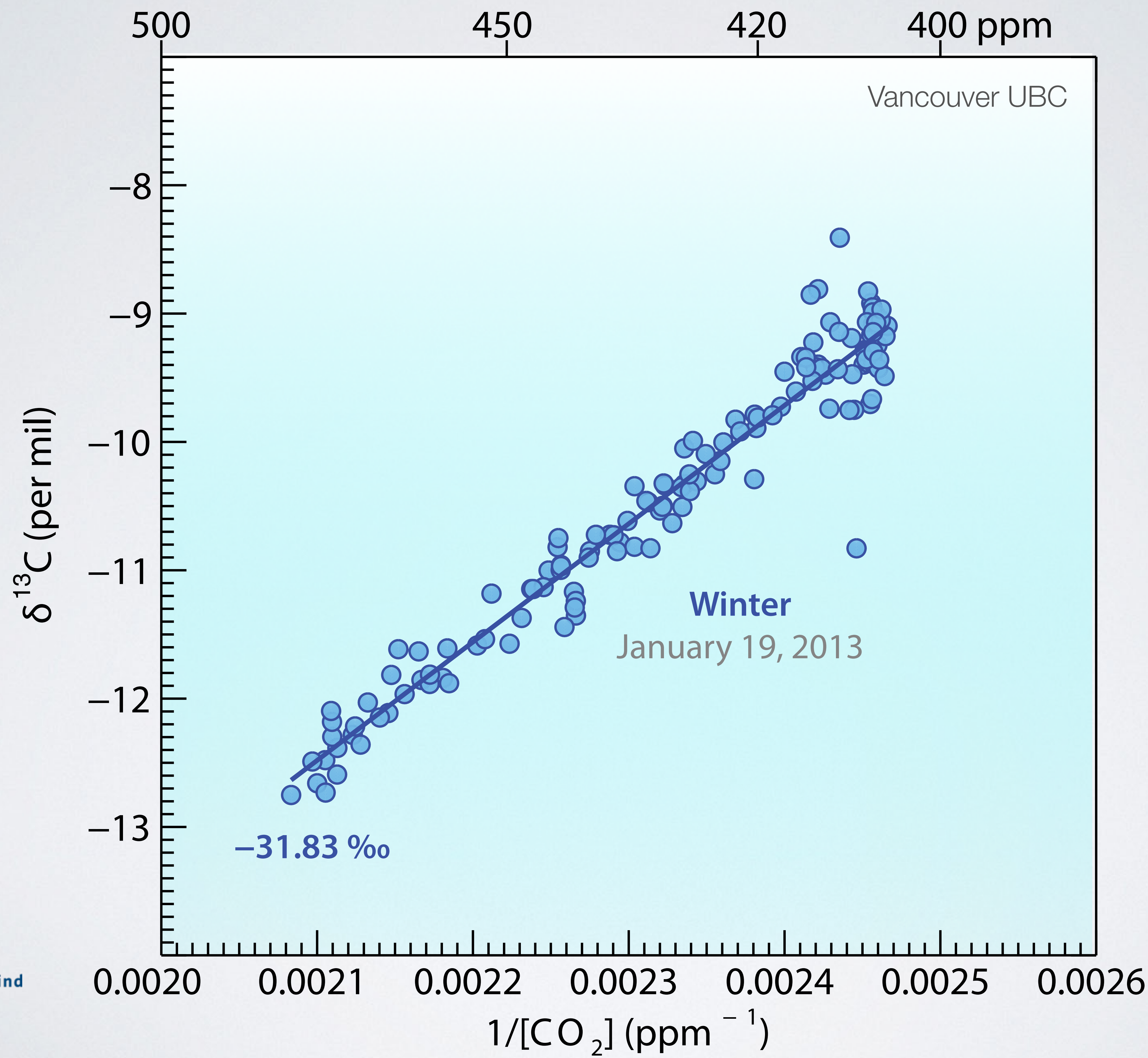
'Keeling plot' for a 24 hour period



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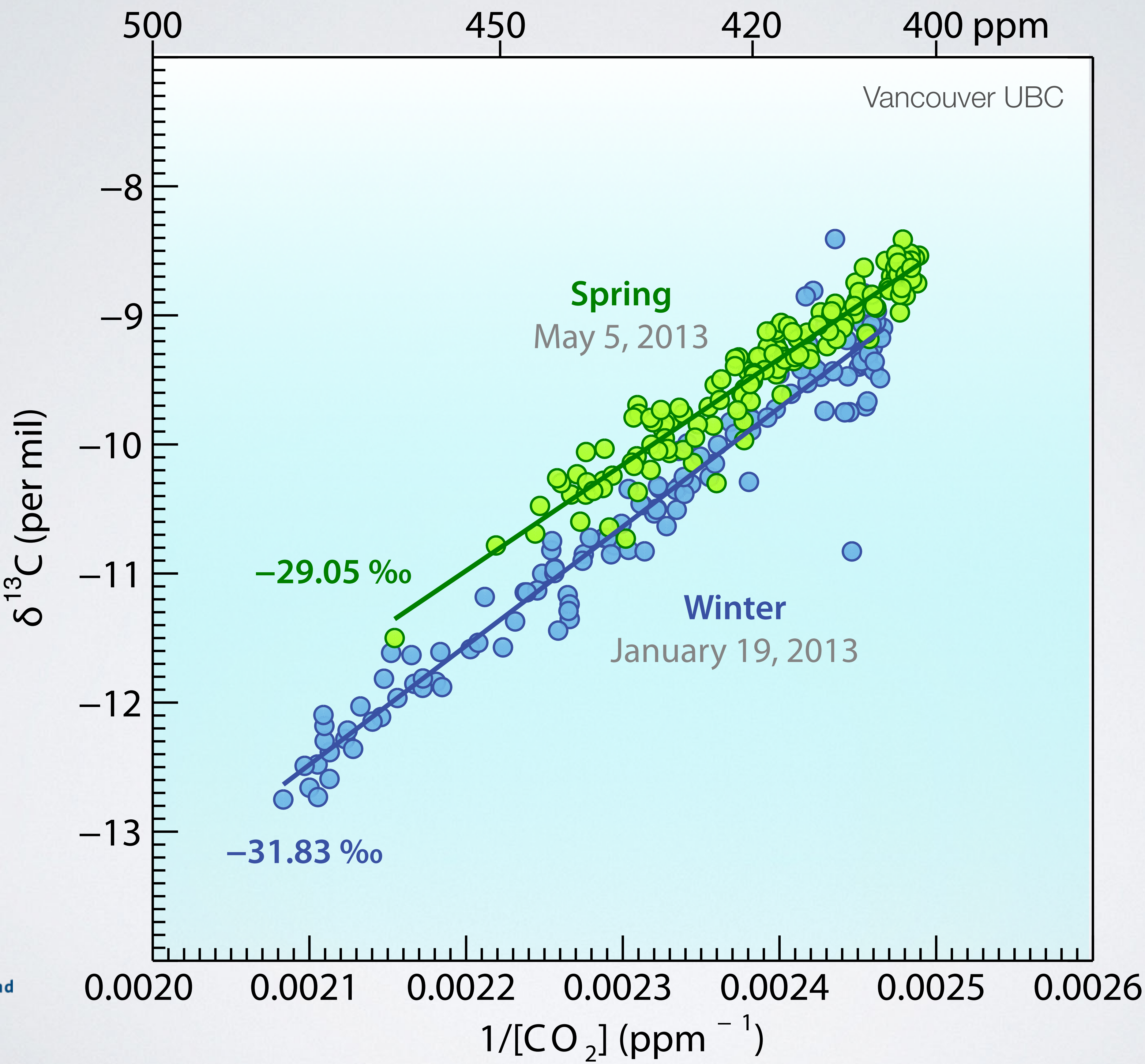
'Keeling plots' for a day in winter and spring



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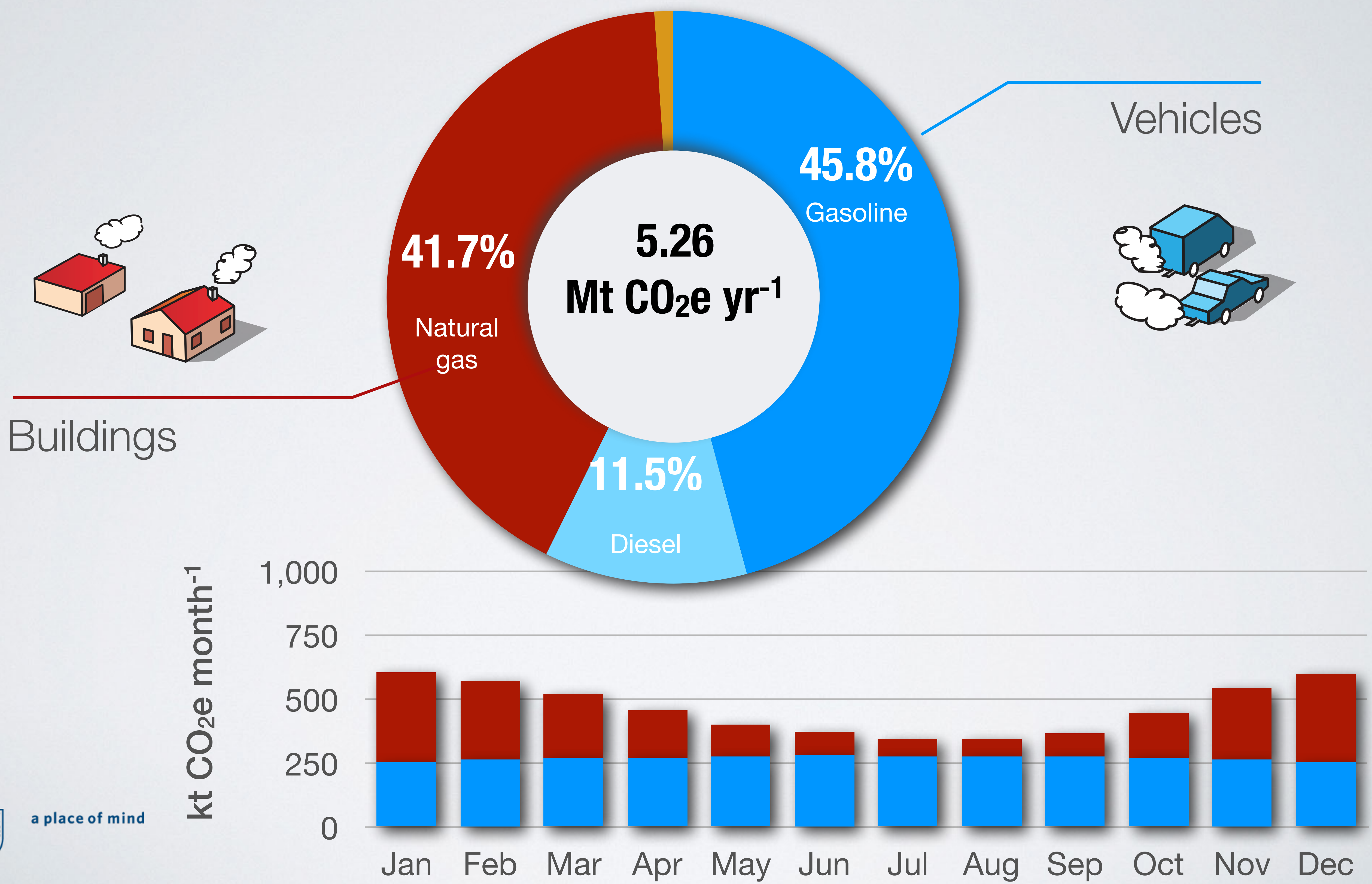
Community Energy and Emissions Inventory



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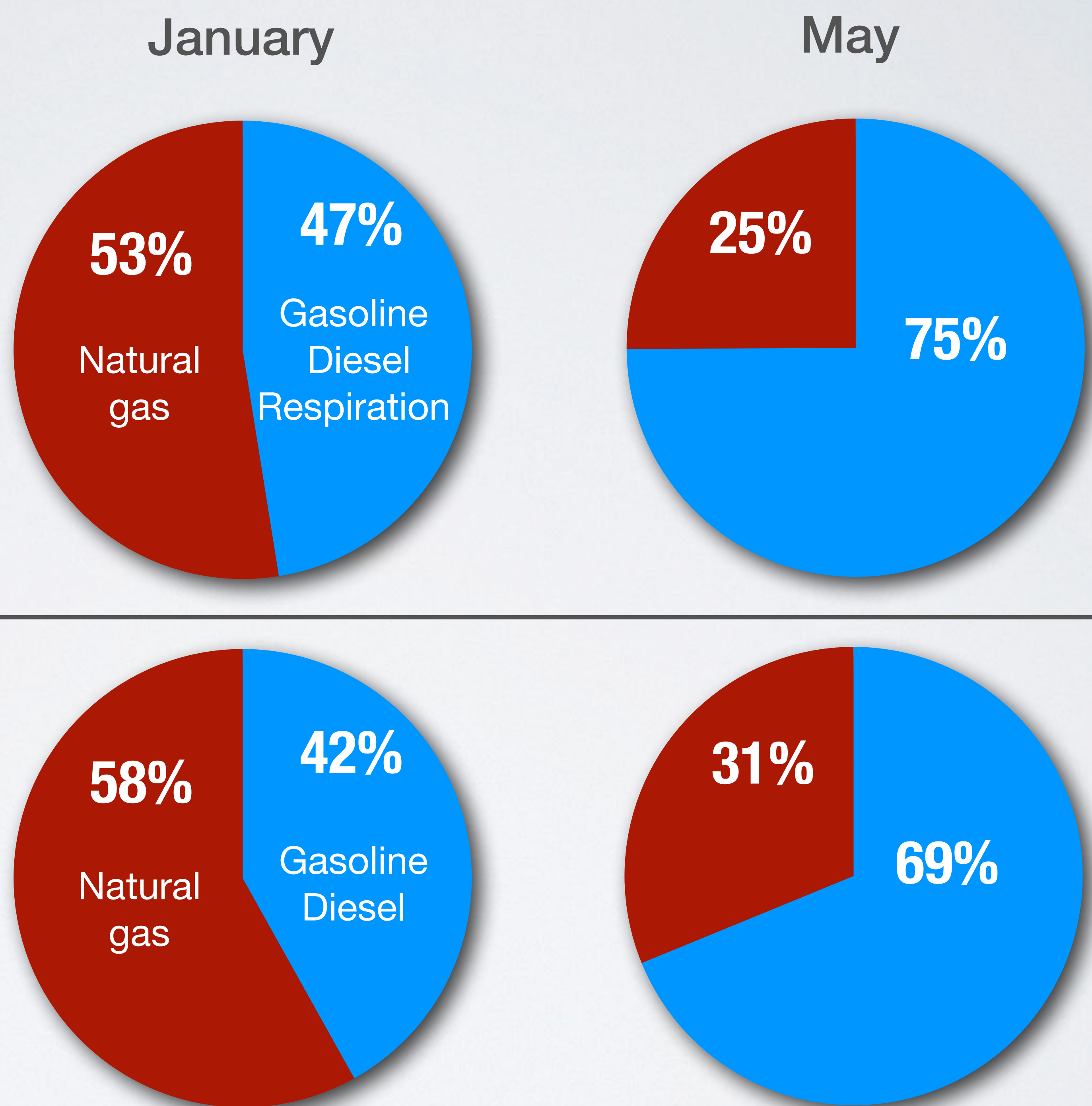
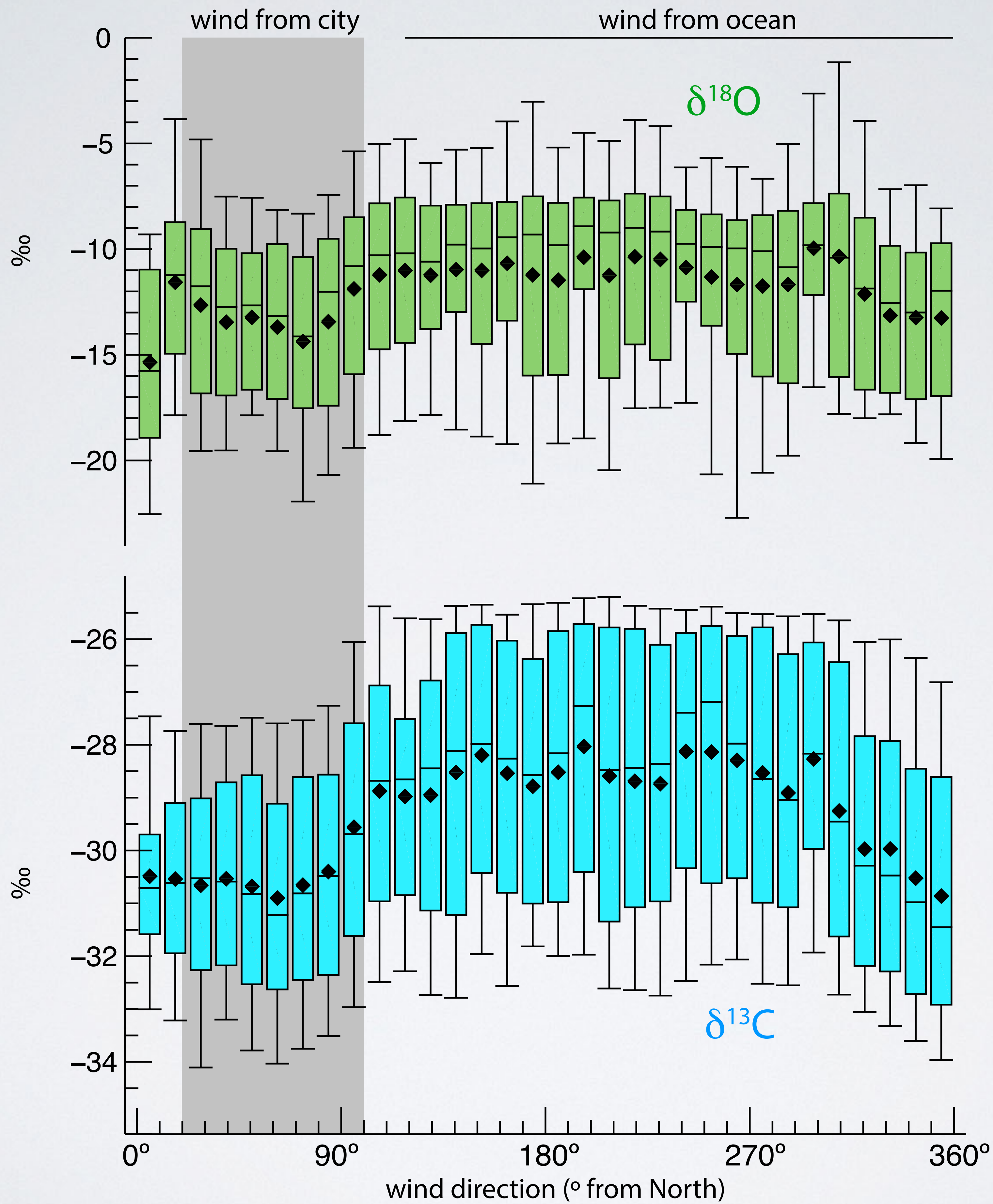
Comparing CEEI and Isotopes

Observation
based on
$\delta^{13}C$ of CO_2
in urban atmosphere

Inventory
Monthly distributed
CEEI / BEM for entire
metropolitan area





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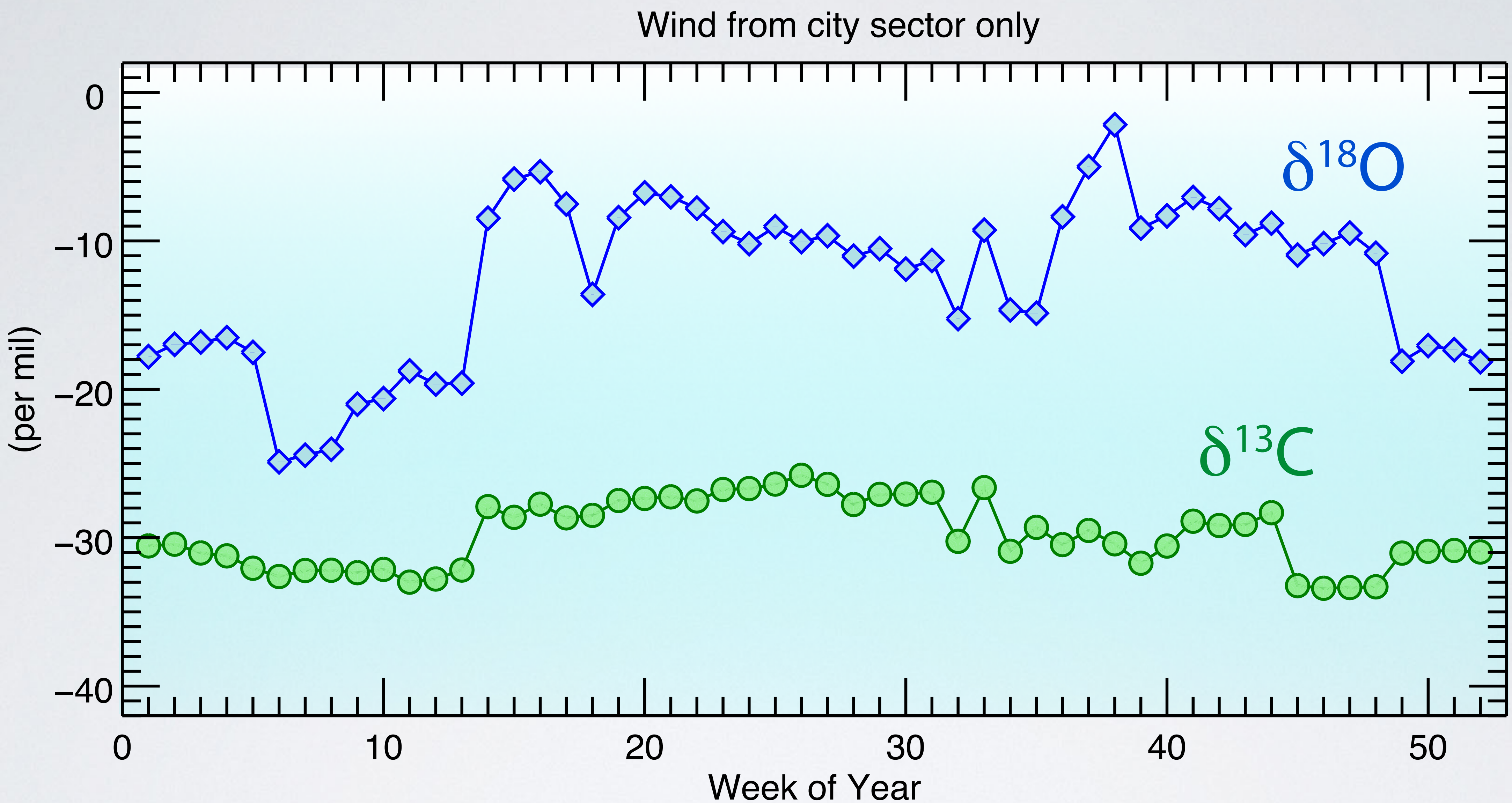
Intercepts change over year



In winter, when there is home heating (natural gas), there is lower $d^{13}C$ and $d^{18}O$ from city sector

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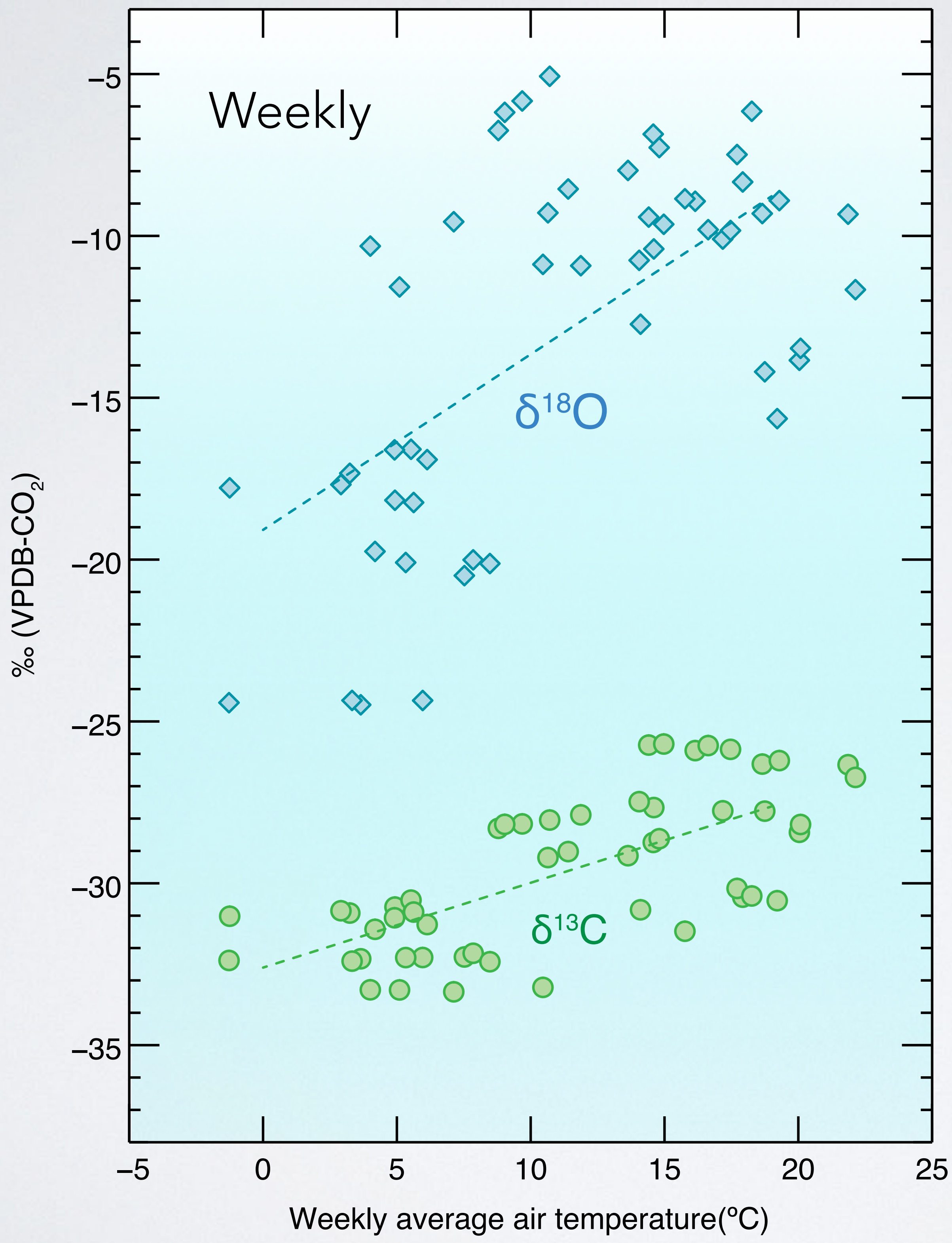
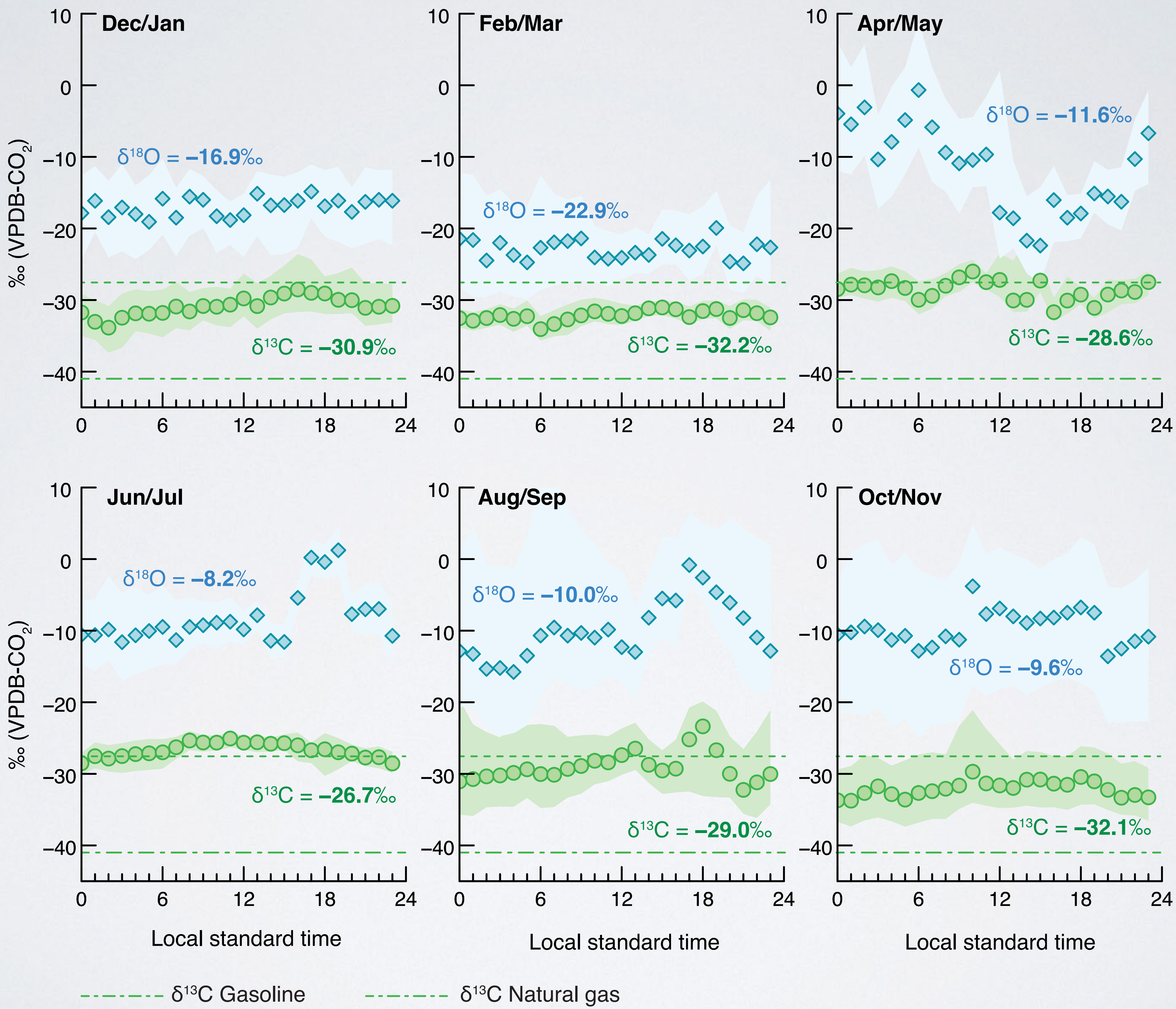
Intercepts are temperature dependent

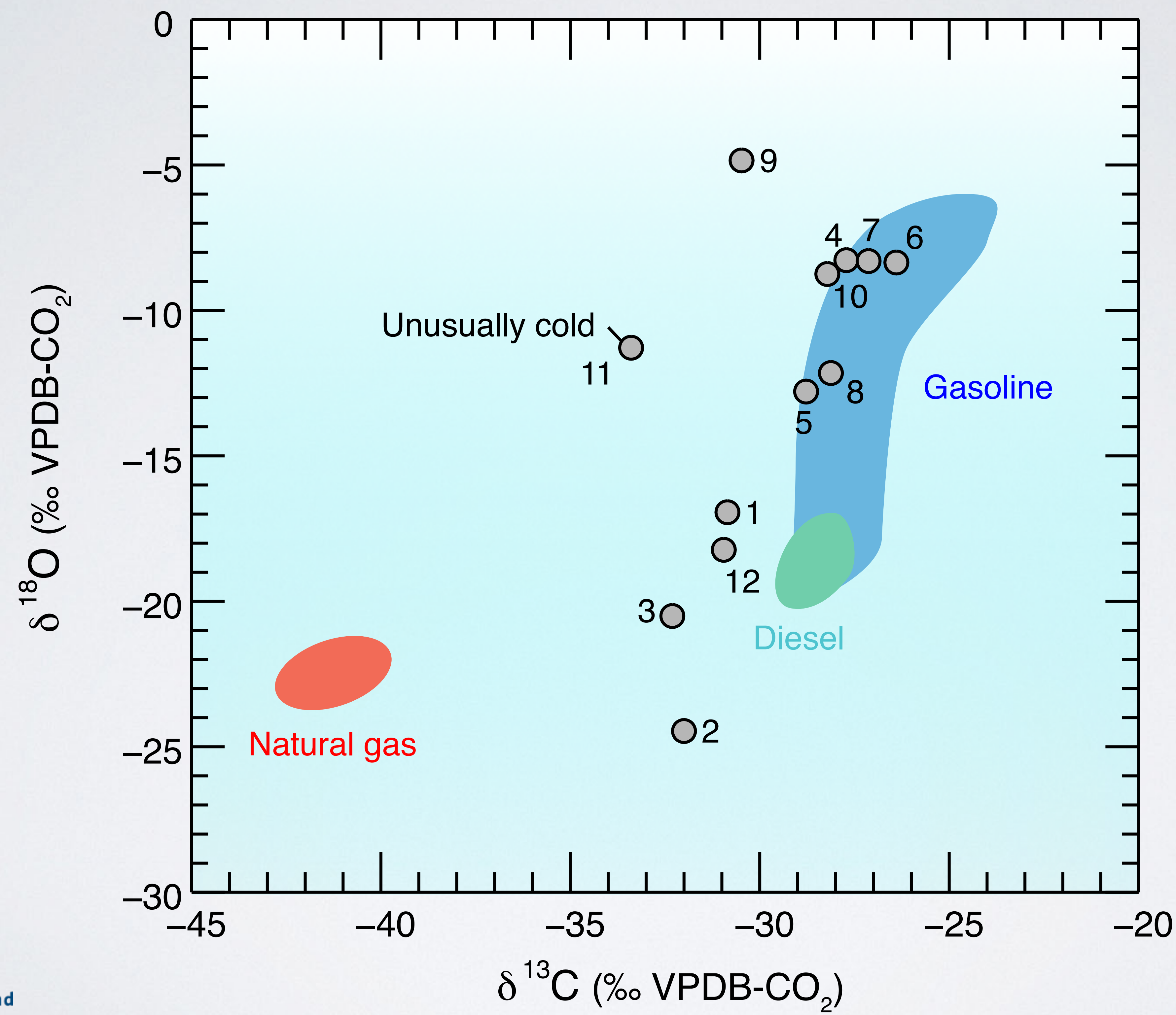


Colder temperatures mean more heating using natural gas (lower $\delta^{13}C$)

Intercepts change over day and year



Annual changes in isotopic signatures



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Summary and conclusions

- 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 $\delta^{18}O$ variations** in gasoline exhaust and respiration and how they vary over the year.
- Explore a **3-end-member mixing model** using $\delta^{13}C$ and $\delta^{18}O$ on seasonal and diurnal scales.
- More carefully characterize **regional background**.
- Future: Develop eddy covariance measurements of CO_2 isotopologues to characterize fleet signatures etc.

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