Greenhouse Gas Source Sector Apportionment with Isotopes and Air Quality Relevant Tracers

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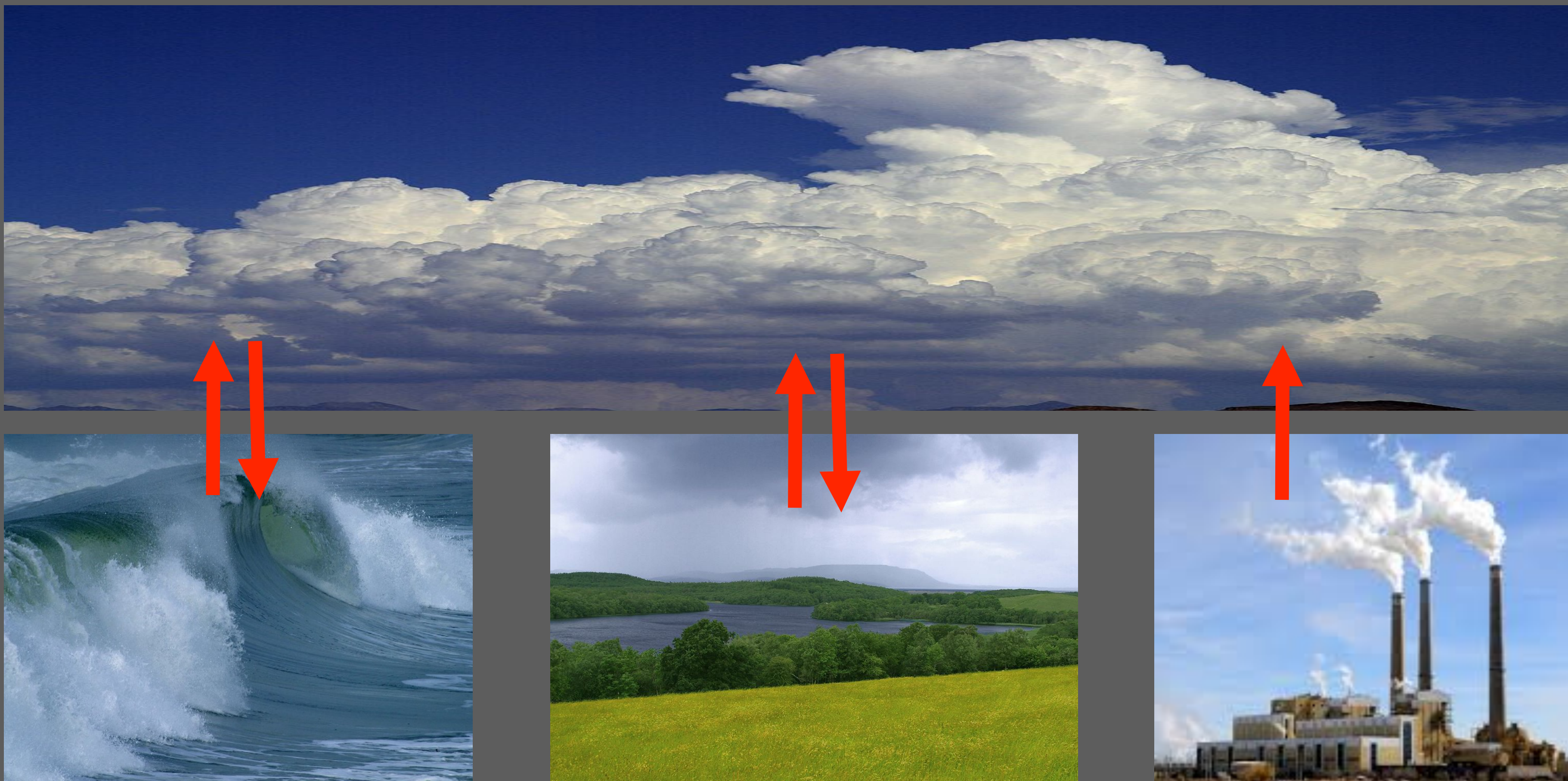
Outline

- Introduction
- Radiocarbon for partitioning fossil and biogenic CO_2
- CO as a correlate tracer for fossil CO_2
- Partitioning petrol/coal/gas with stable isotopes
- Other tracers

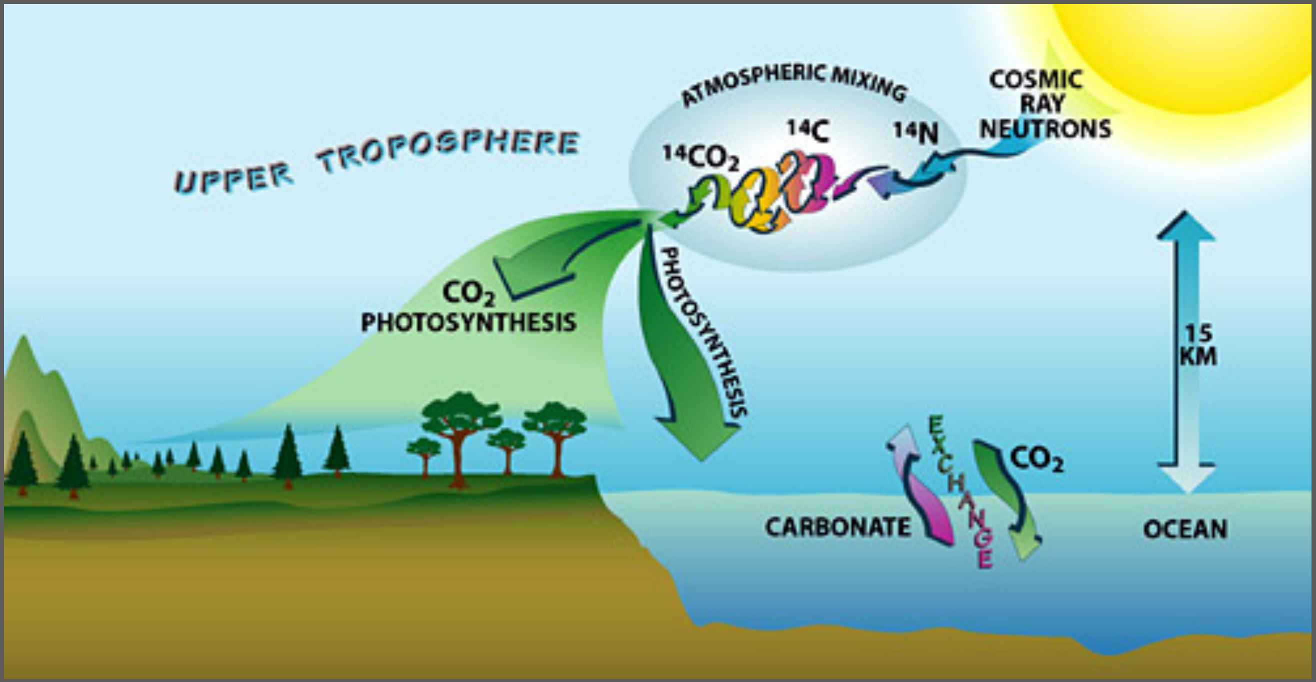
The Global Carbon Cycle

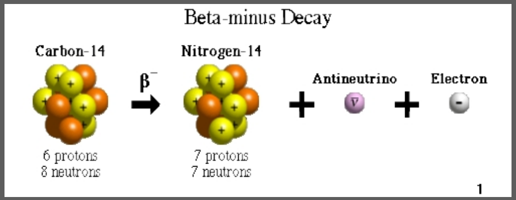


The Urban Carbon Cycle

Can we apportion urban emissions to different source sectors?

Radiocarbon (^{14}C) dating





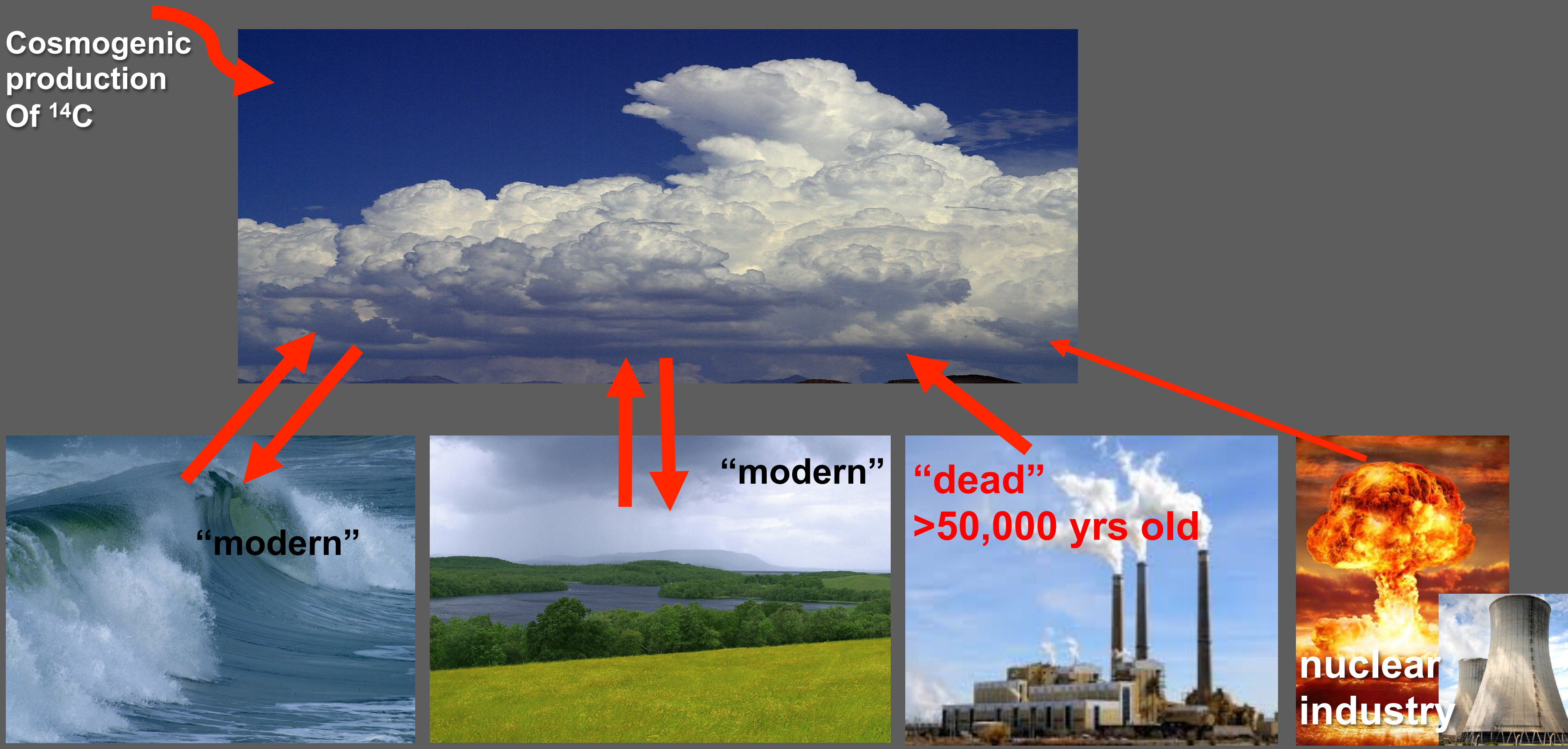
^{14}C is produced naturally in the atmosphere, and moves throughout the carbon cycle

Natural radioactive decay removes ^{14}C from buried/dead objects

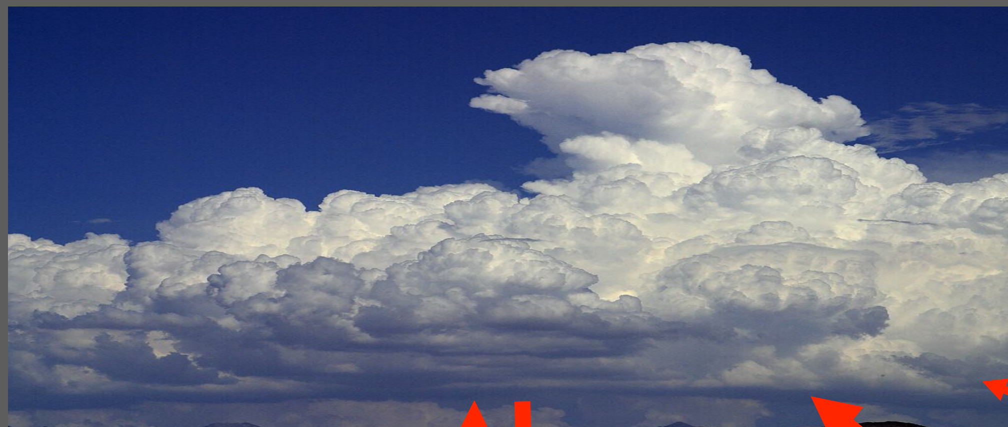
Half-life 5,700 years

Fossil fuels are entirely devoid of ^{14}C

The Global Radiocarbon Cycle

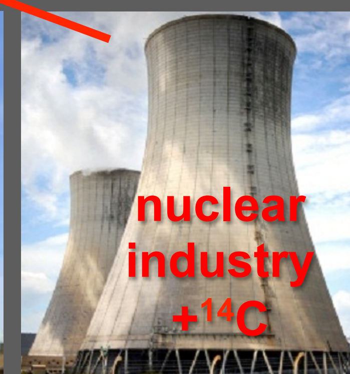


The Urban Radiocarbon Cycle



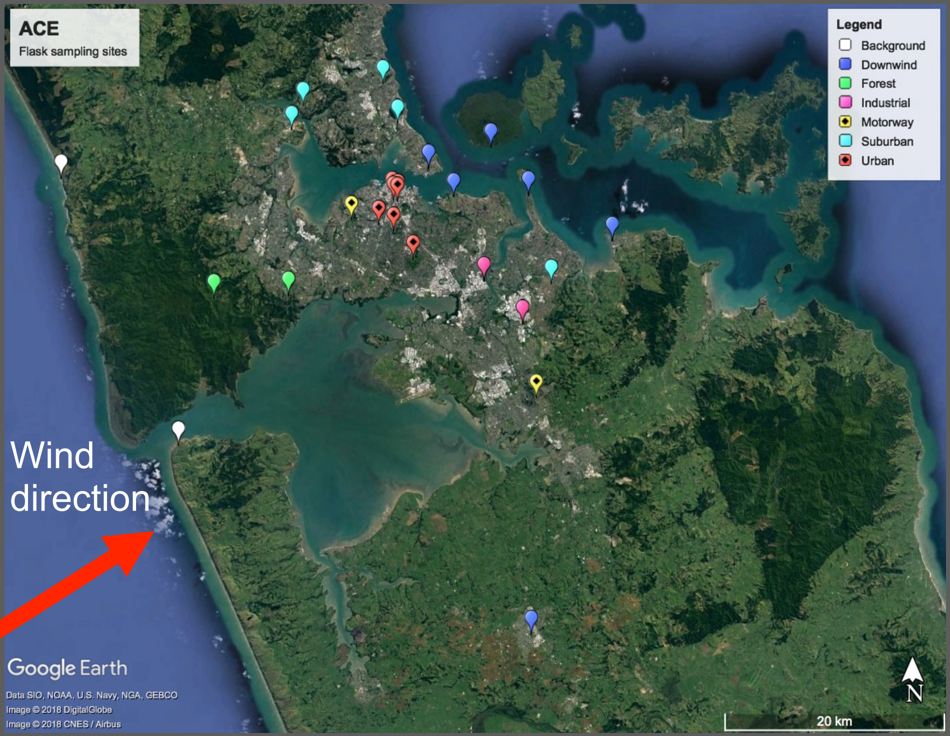
$^{14}CO_2$ separates fossil fuel CO_2 from natural CO_2

-2.7‰ change in $\Delta^{14}C$ for each 1 ppm fossil fuel CO_2 added



$$CO_2ff = \frac{CO_{2obs}(\Delta_{obs} - \Delta_{bg})}{\Delta_{ff} - \Delta_{bg}} - \frac{CO_{2r}(\Delta_r - \Delta_{bg})}{\Delta_{ff} - \Delta_{bg}}$$

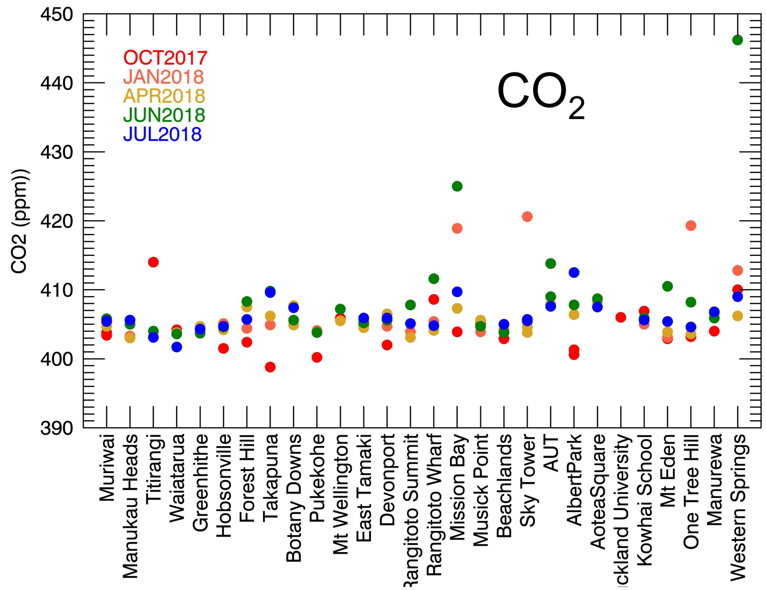
Partitioning fossil fuel and biogenic CO_2 with ^{14}C in Auckland, New Zealand

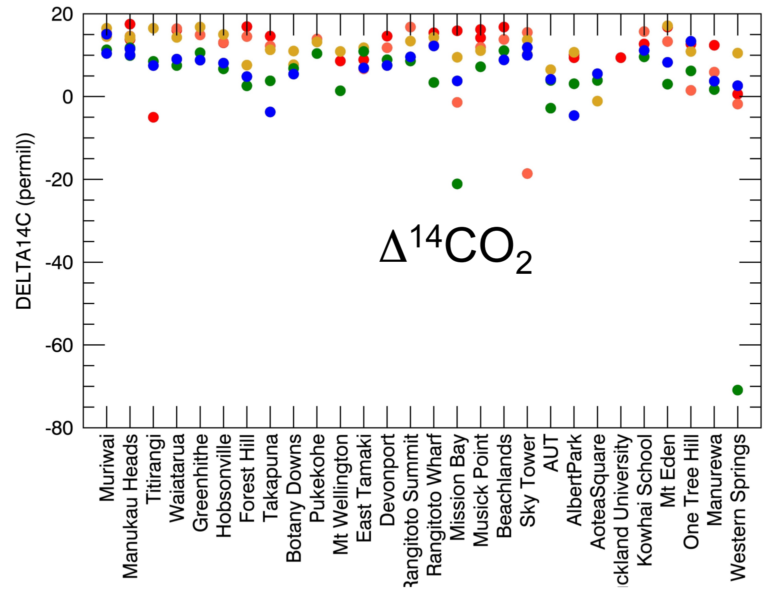


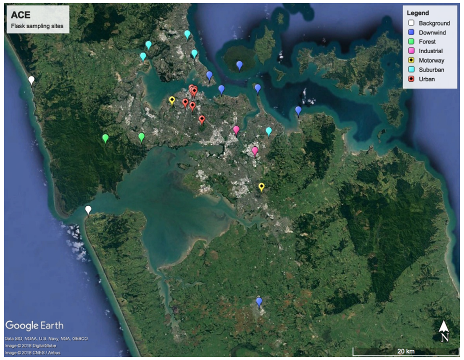
Grab flask samples from ~26 sites

4 sampling campaigns per year

Auckland flask results

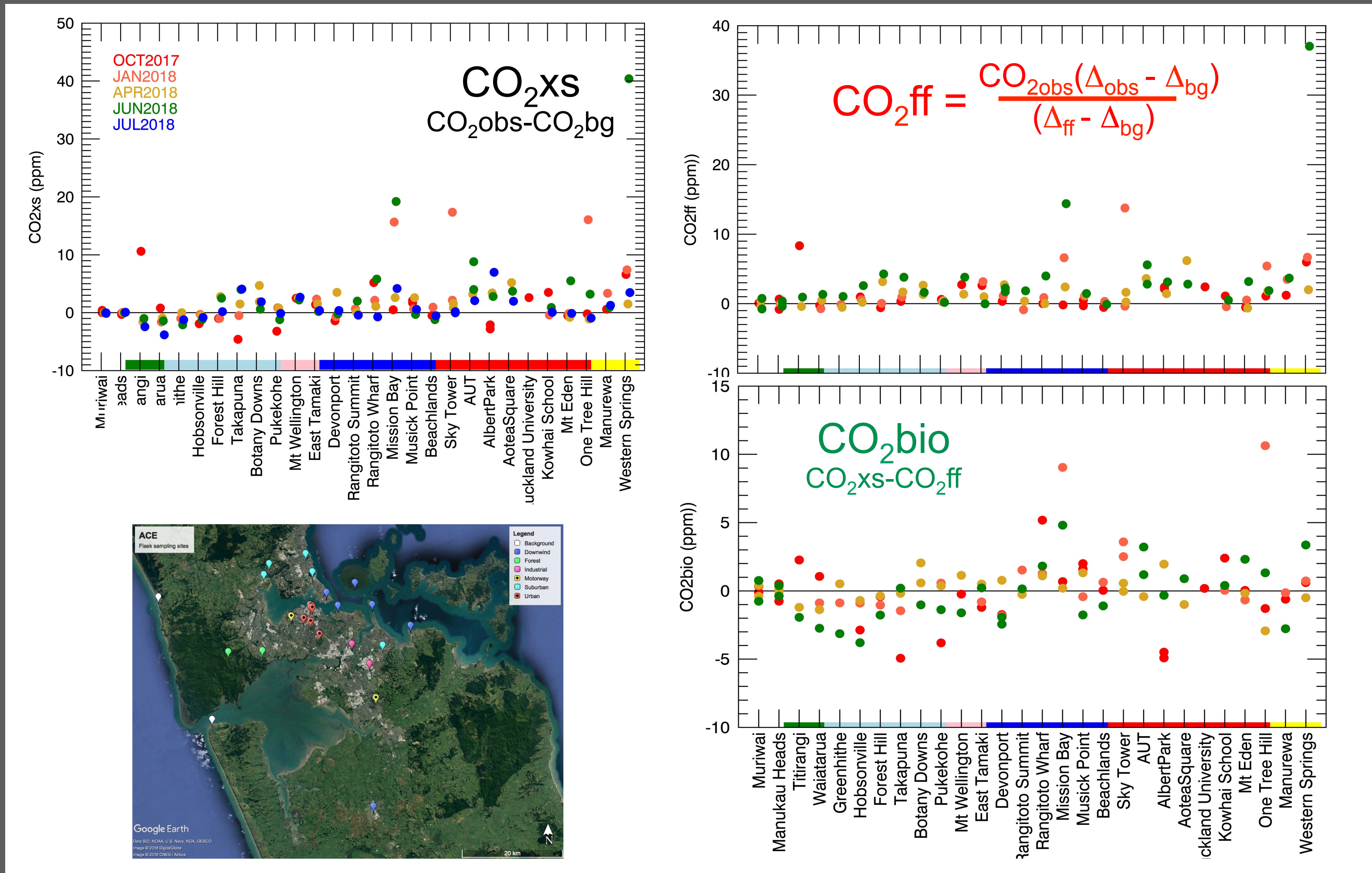






$$CO_{2ff} = \frac{CO_{2obs}(\Delta_{obs} - \Delta_{bg})}{(\Delta_{ff} - \Delta_{bg})}$$

Auckland flask results



High CO_2ff and CO values at urban, industrial, motorway sites

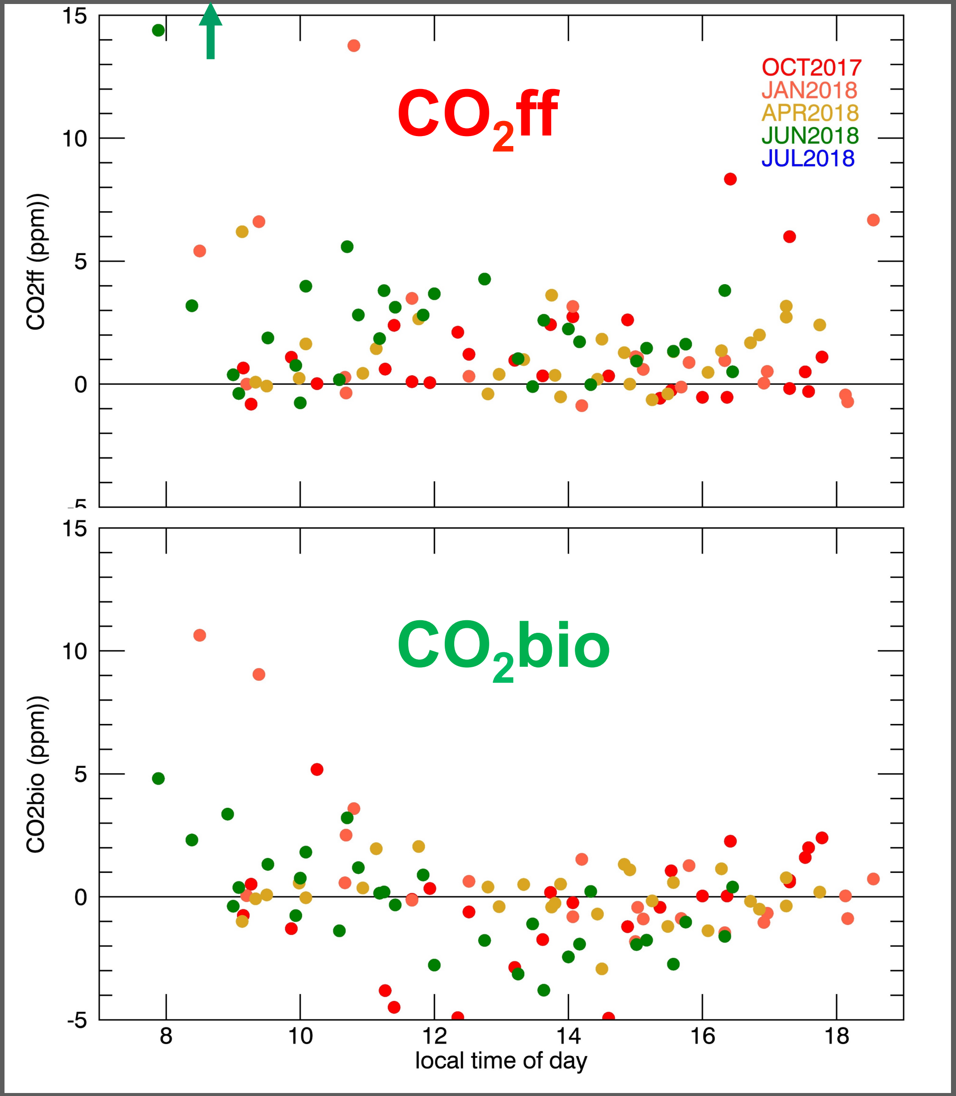
CO_2bio often negative

Auckland flask results

No pattern in CO_2ff by time of day

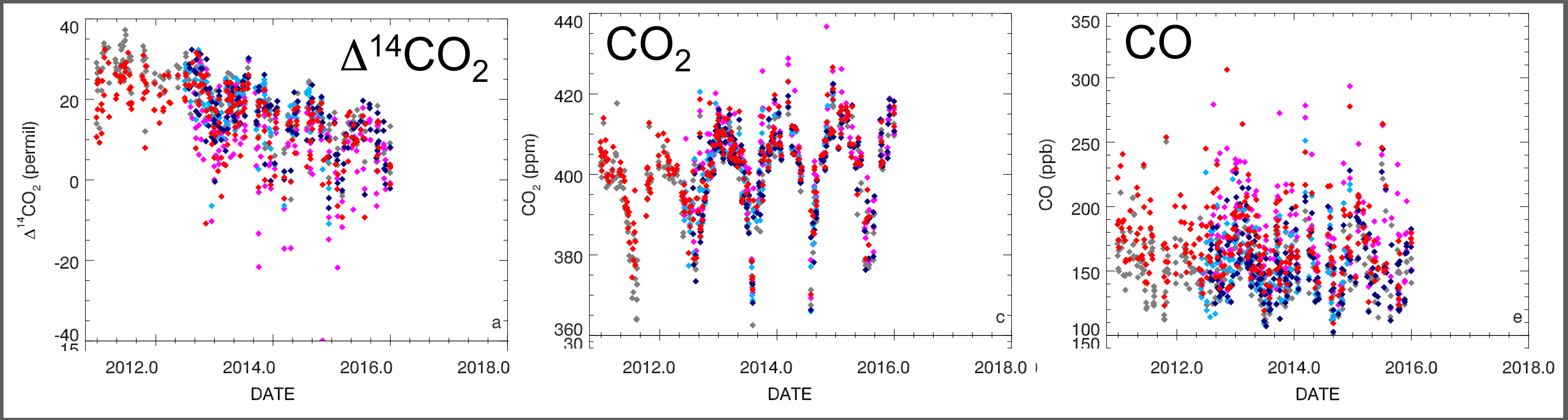
Clear but variable afternoon drawdown in CO_2bio

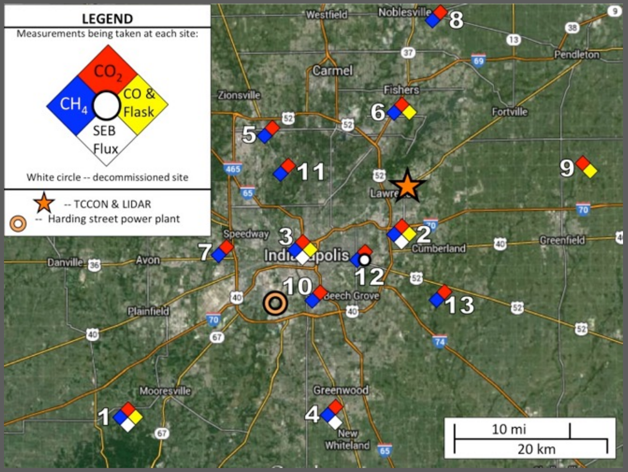
Daytime drawdown of similar magnitude to CO_2ff



CO correlate tracer linked to ^{14}C

Flask-based estimates of CO and CO_2ff

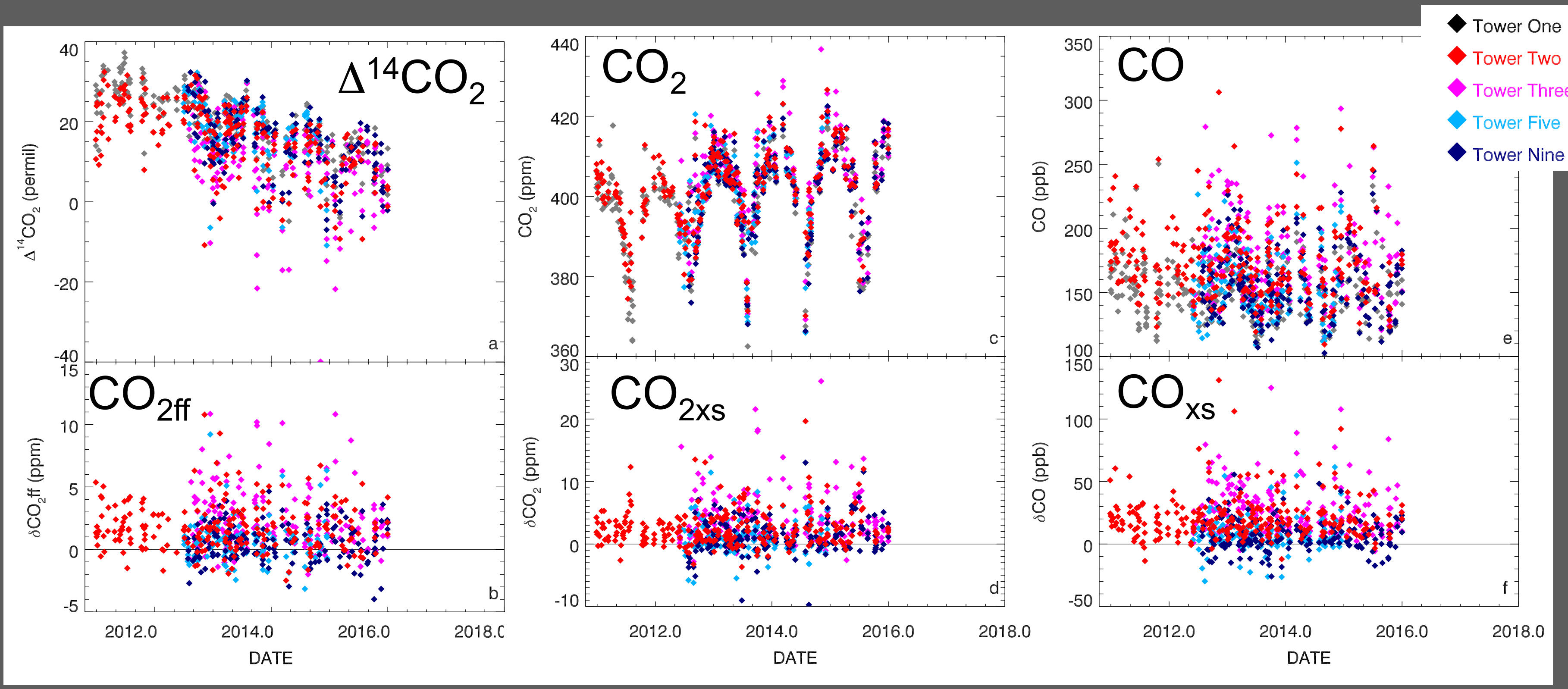




- Tower One
- Tower Two
- Tower Three
- Tower Five
- Tower Nine

Flask measurements at towers (and from aircraft) around Indianapolis

Flask-based estimates of CO and CO_2ff

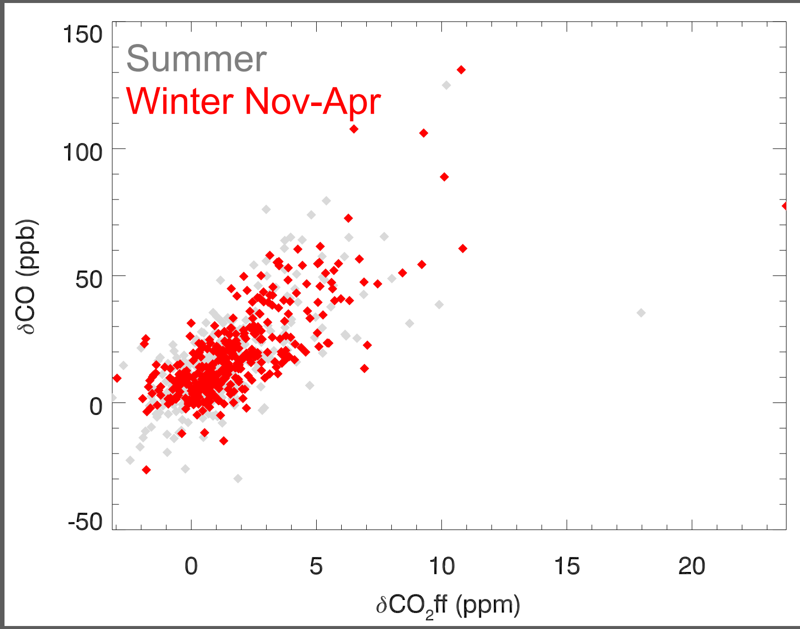


$$CO_{2ff} = \frac{CO_{2obs}(\Delta_{obs} - \Delta_{bg})}{(\Delta_{ff} - \Delta_{bg})}$$

Consistent enhancements in anthropogenic species at downwind towers

Turnbull et al., 2015

Flask-based estimates of CO and CO_2ff

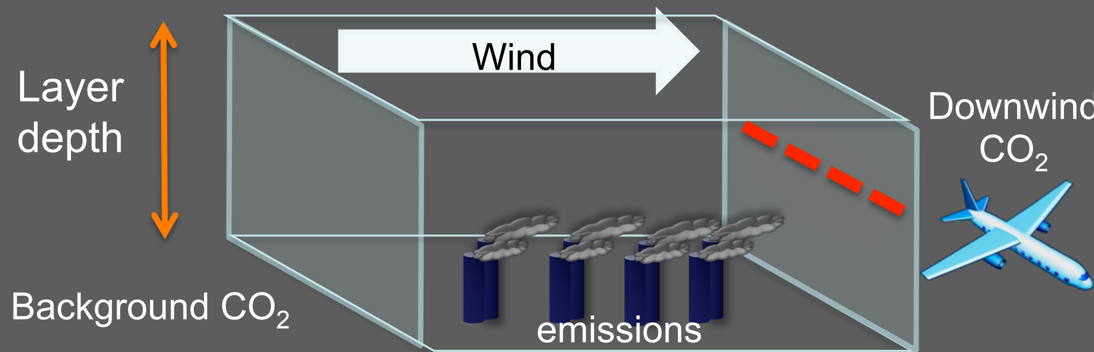


	R_{CO} (ppb/ppm)
Towers Winter Nov-Apr	7 ± 2
Aircraft winter	9 ± 2
Towers summer	8 ± 1
Aircraft summer	8 ± 1

CO co-emitted with CO_2ff at variable rate depending on combustion conditions

Empirically derive $R_{CO} = CO/CO_2ff$

Urban mass balance from aircraft measurements

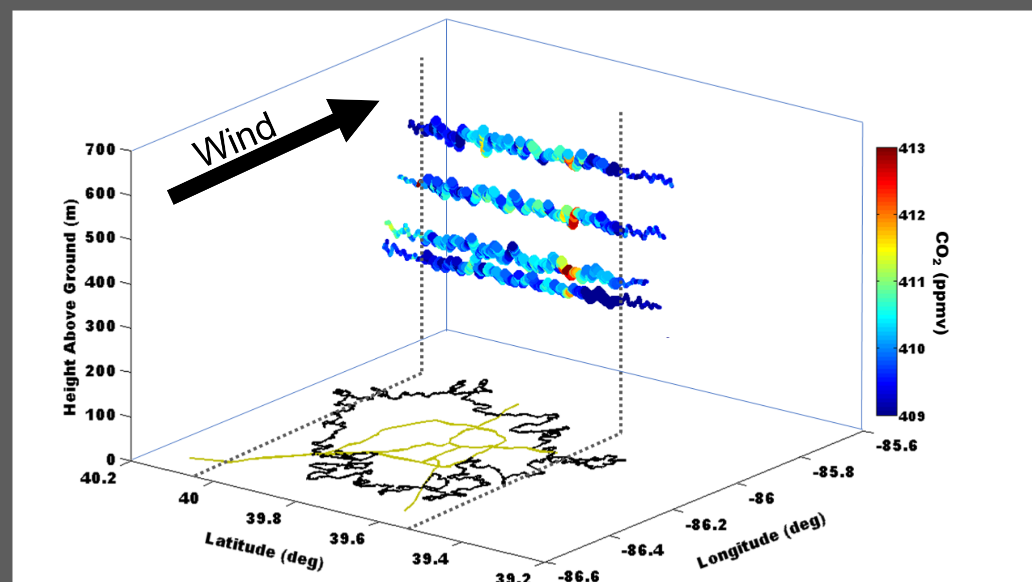


Flux

Molar enhancement in air layer

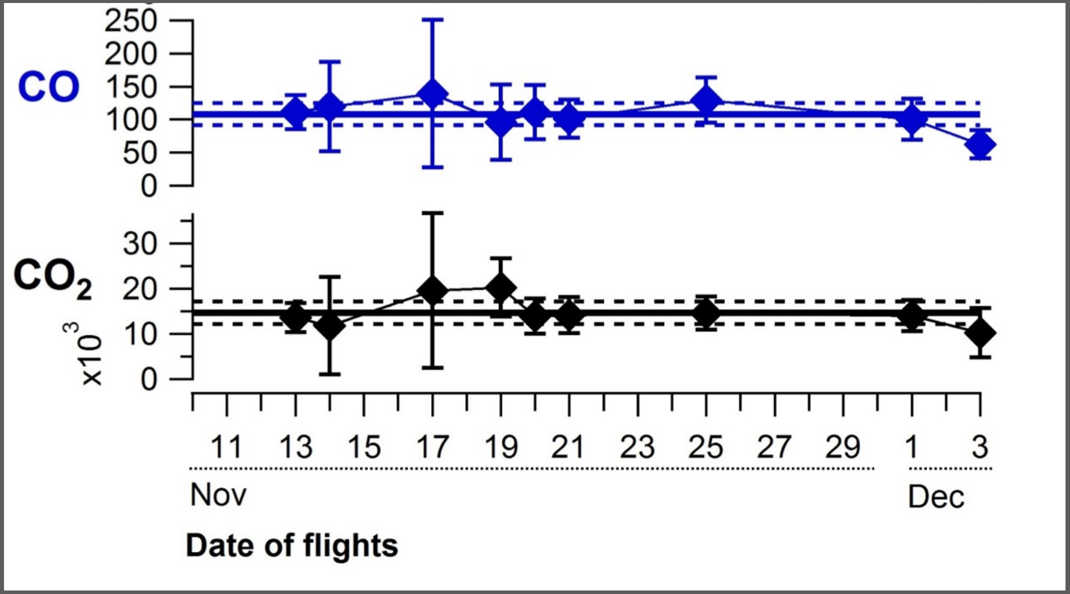
$$\dot{n}_{CO_2} = V\cos\theta \int_{-b}^{+b} \Delta X_{CO_2} \left(\int_{z_{gnd}}^{z_{PBL}} n_{air}\, dz \right) dx$$

Perpendicular wind speed



Heimburger et al., 2017

Urban mass balance from aircraft measurements



Calculate flux for nine flights in Nov-Dec 2014

Estimate uncertainty from scatter of the nine results

Calculate for both CO_2 and carbon monoxide (CO)

	Emission rate (mol/s)
CO winter 2014	108 ± 16%
CO_2 winter 2014	14,600 ± 17%

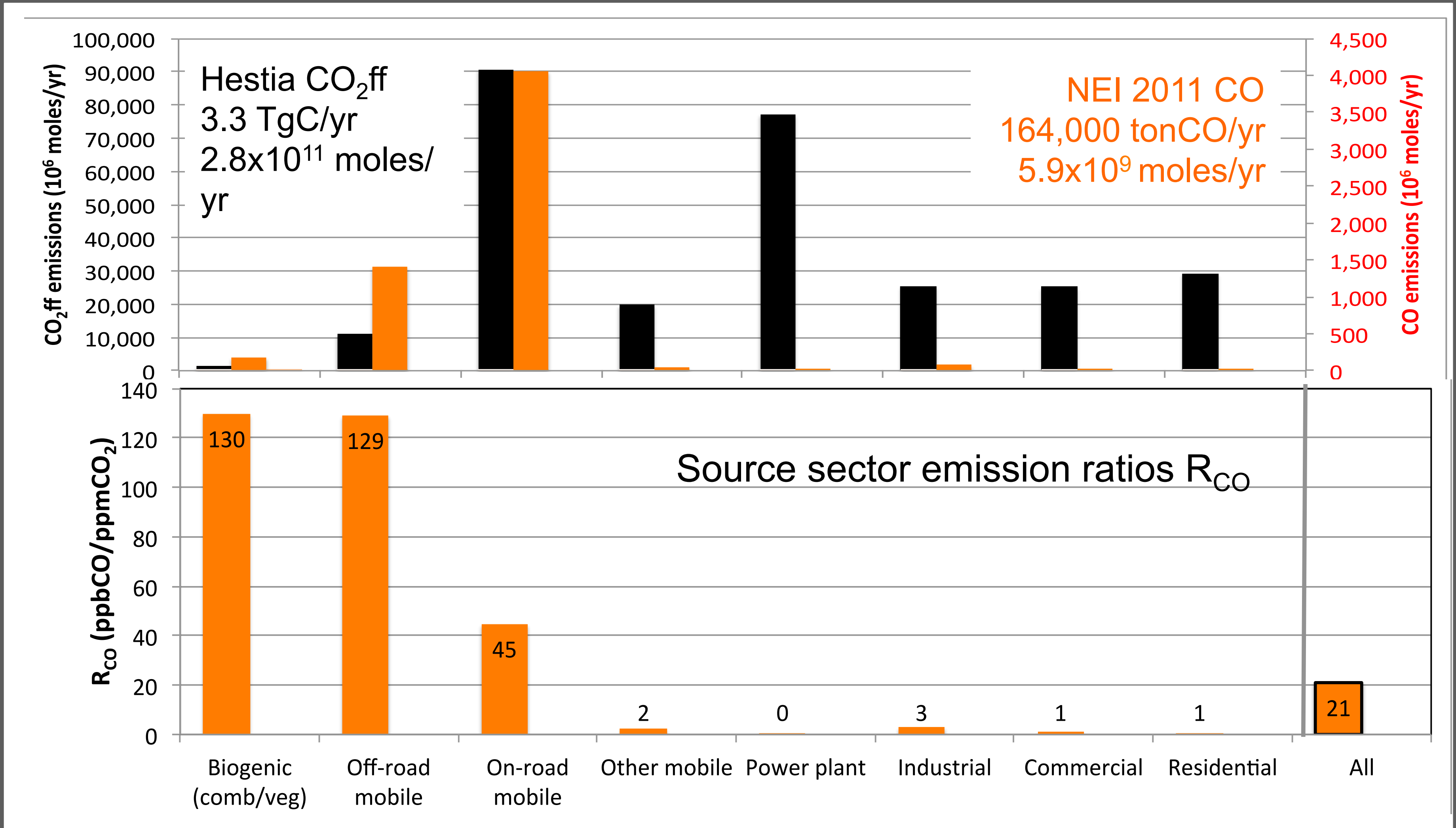
7 ± 2 ppbCO/ppmCO_2ff

Indianapolis CO_2ff emission rate 15,400 ± 21%

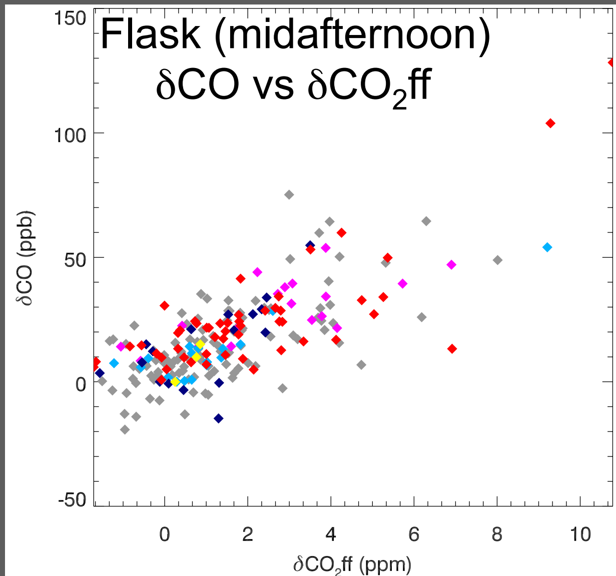
Heimburger et al., 2017

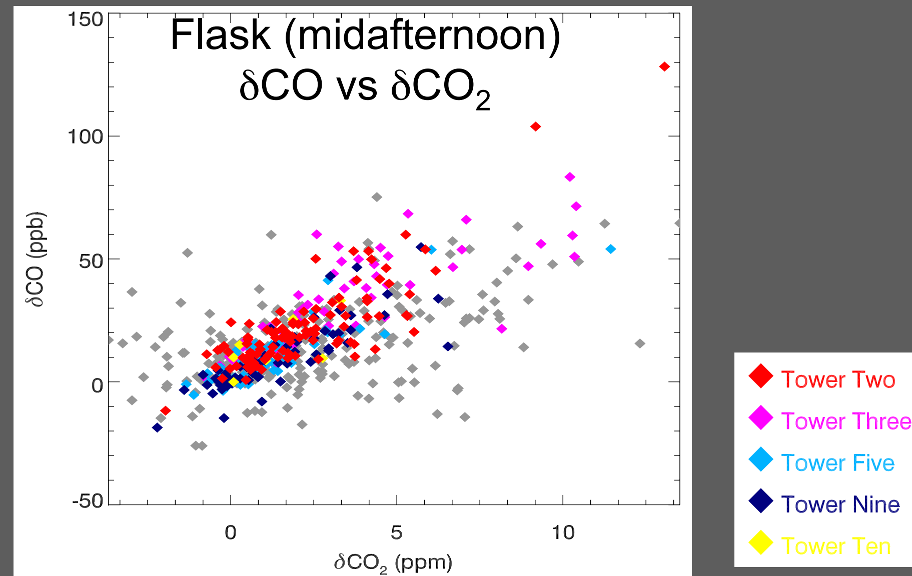
Evaluate reported urban CO emission rate

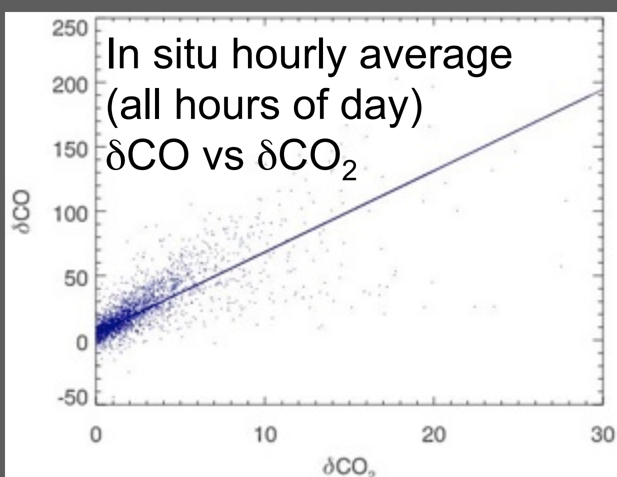
CO and CO_2ff emissions by source sector



Validating bottom-up CO inventory with observed R_{CO}



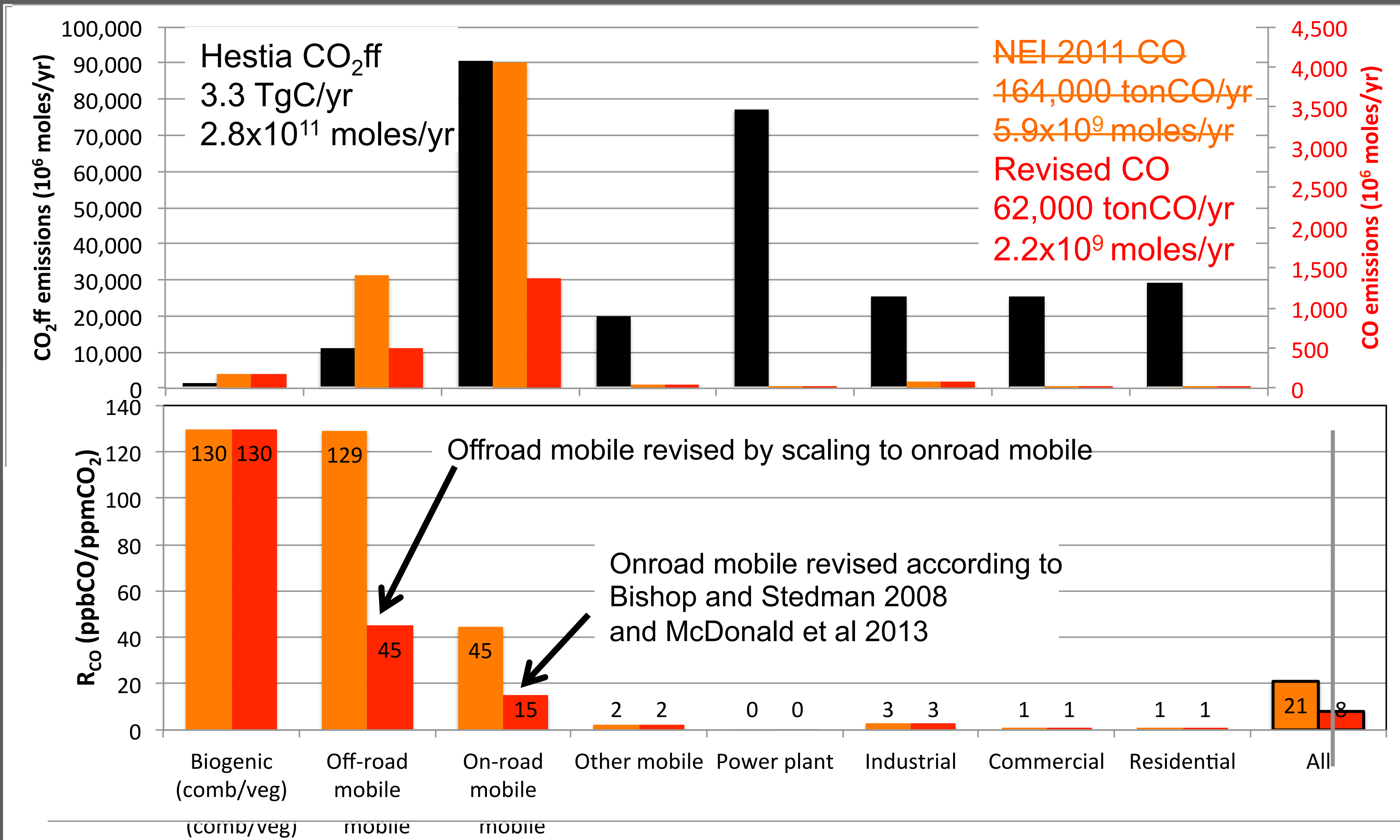




Winter correlations	**Slope R_{CO} (ppb/ppm)**		
	Flask $CO:CO_2ff$	Flask $CO:CO_2$	In situ $CO:CO_2$
Observations	7 ± 1	6 ± 1	7 ± 1
Bottom-up NEI 2011	**21**		

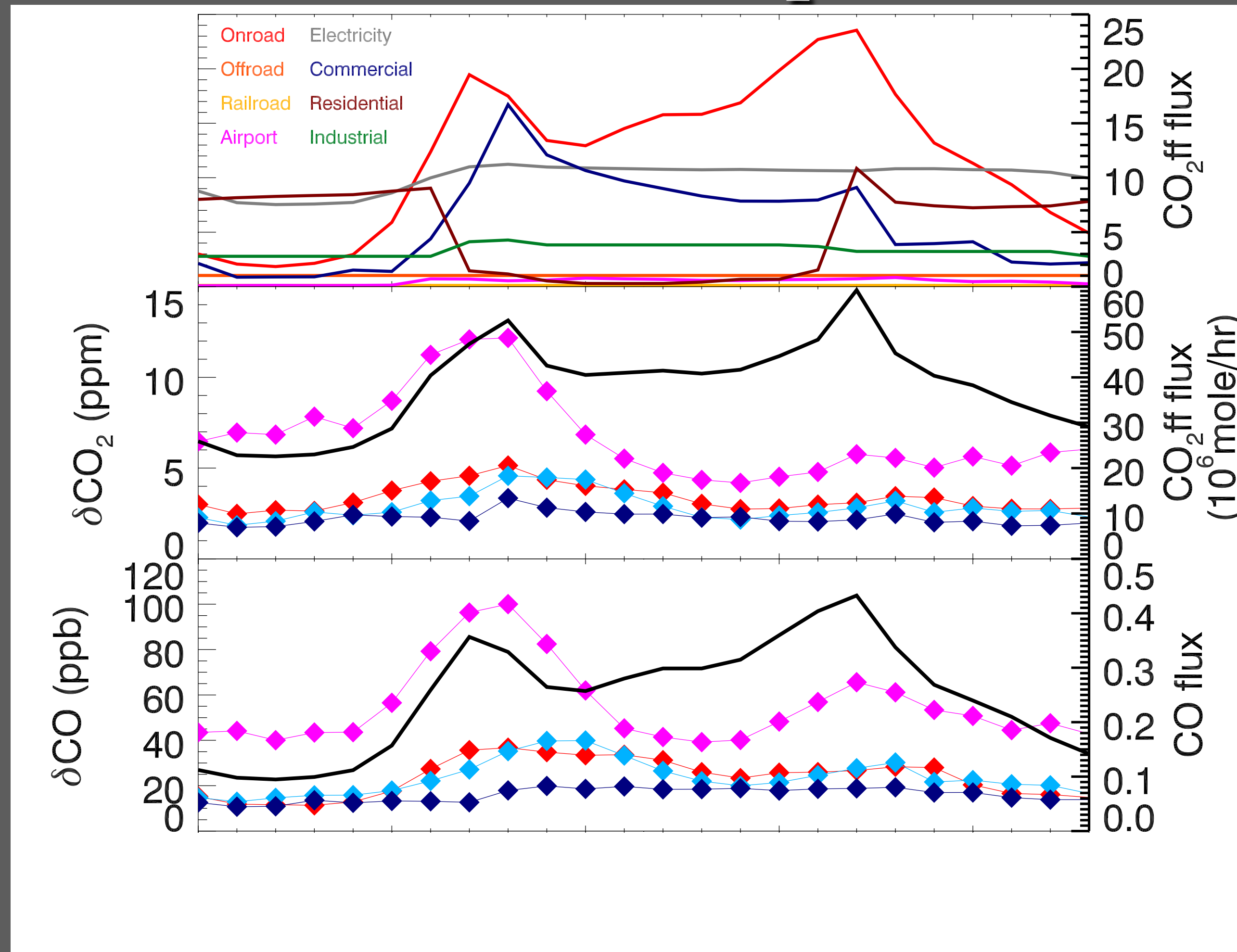
Bottom-up NEI 2011 CO inventory appears to be ~3x too large

Revised CO emissions and emission ratios



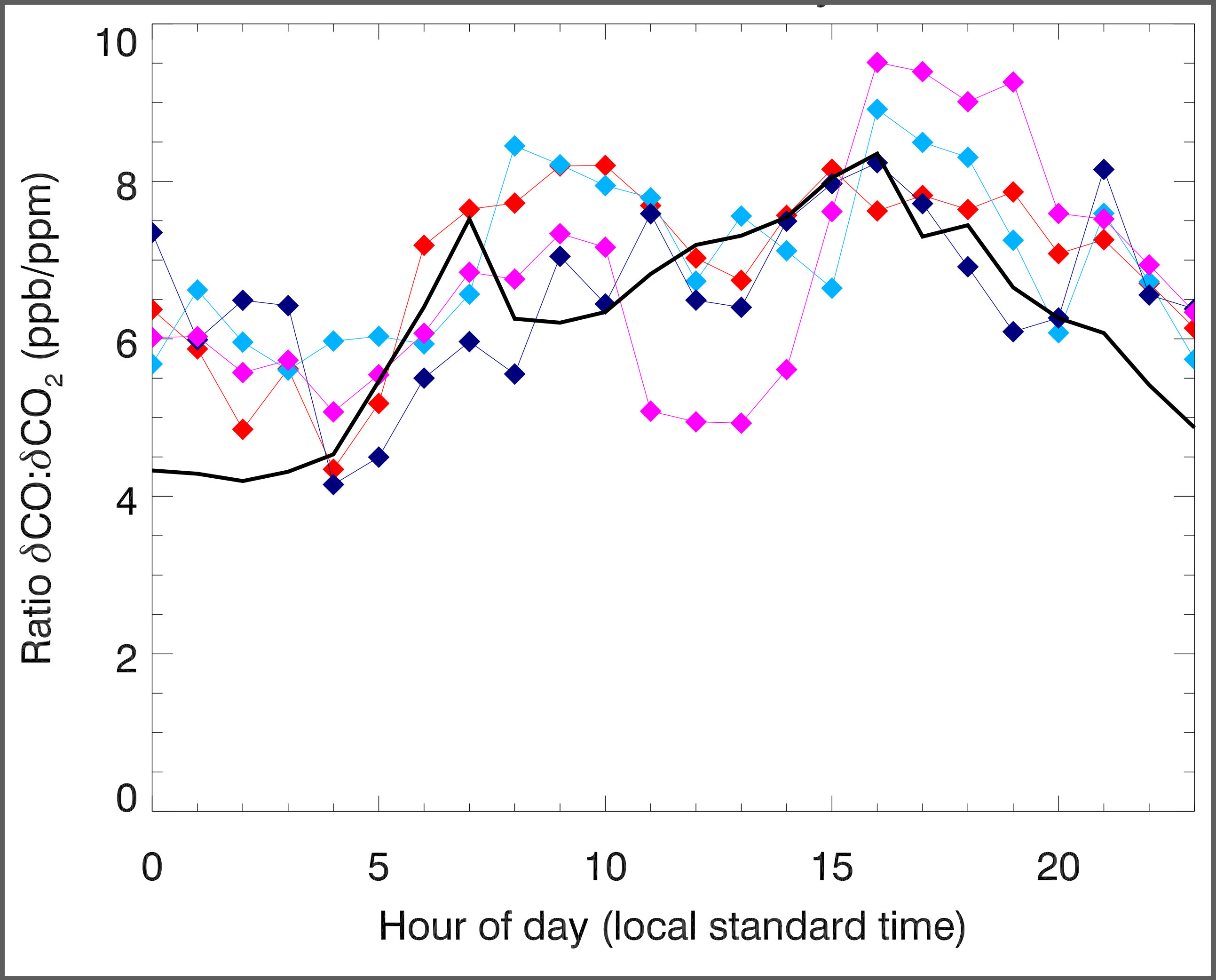
Evaluate relative source sector contributions to CO_2ff

Bottom-up emission rates and observed mole fractions for CO and CO_2



Indirect relationship between emission flux and observed enhancement

Weekday bottom-up and in situ observed diurnal R_{CO}

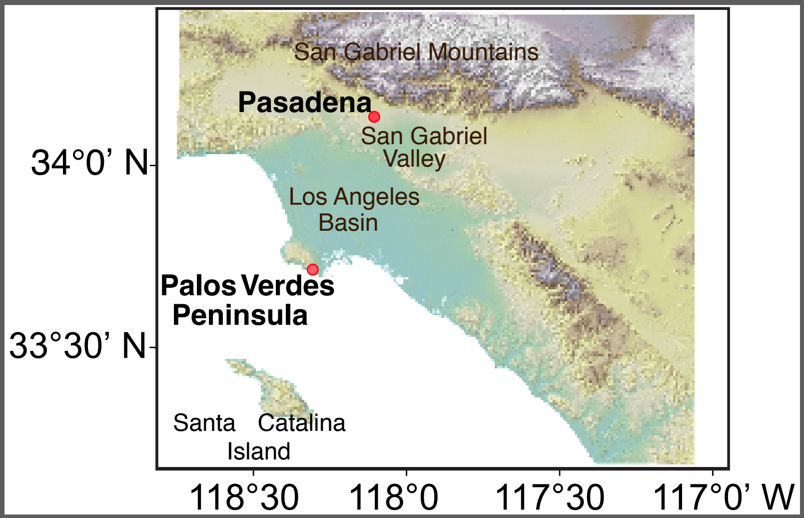


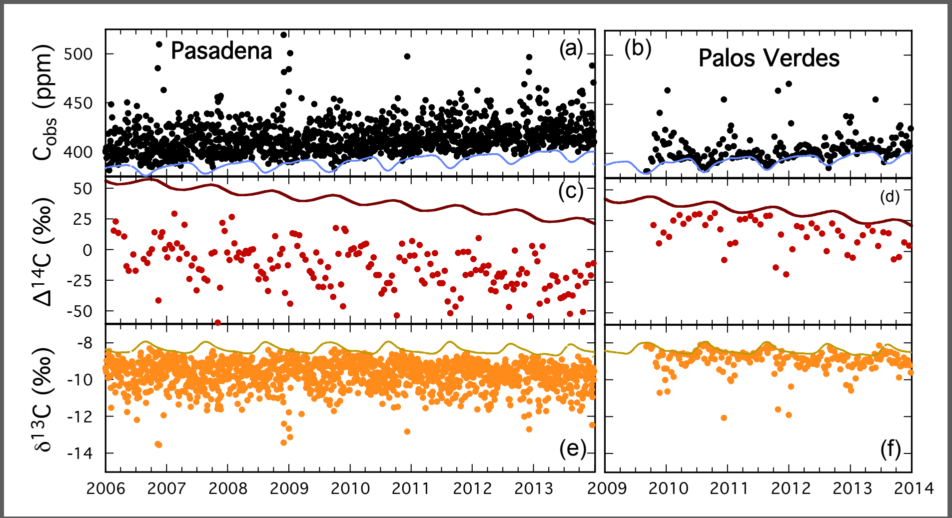
Direct relationship between bottom-up and top-down ratios

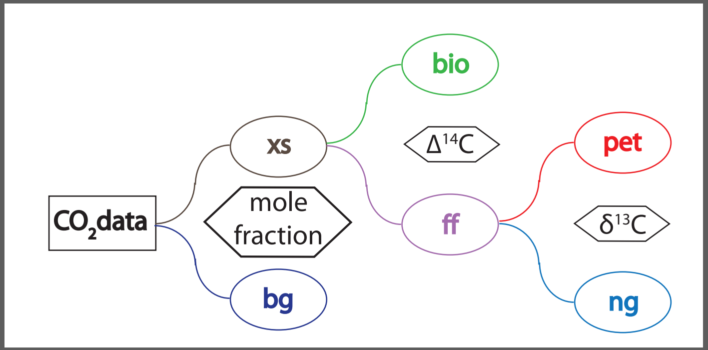
Partitioning by fossil fuel type with ^{13}C

Partitioning by fossil fuel type with ^{13}C

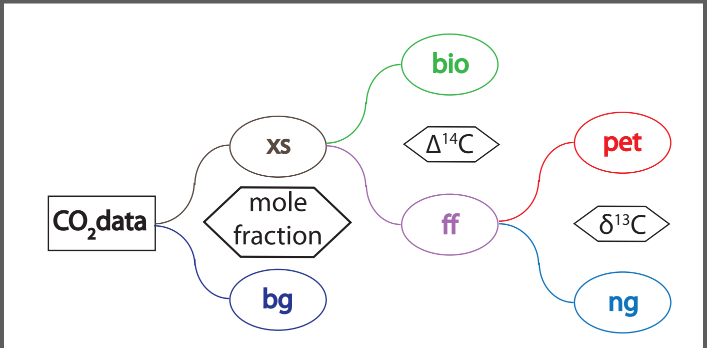
Los Angeles, Newman et al 2016

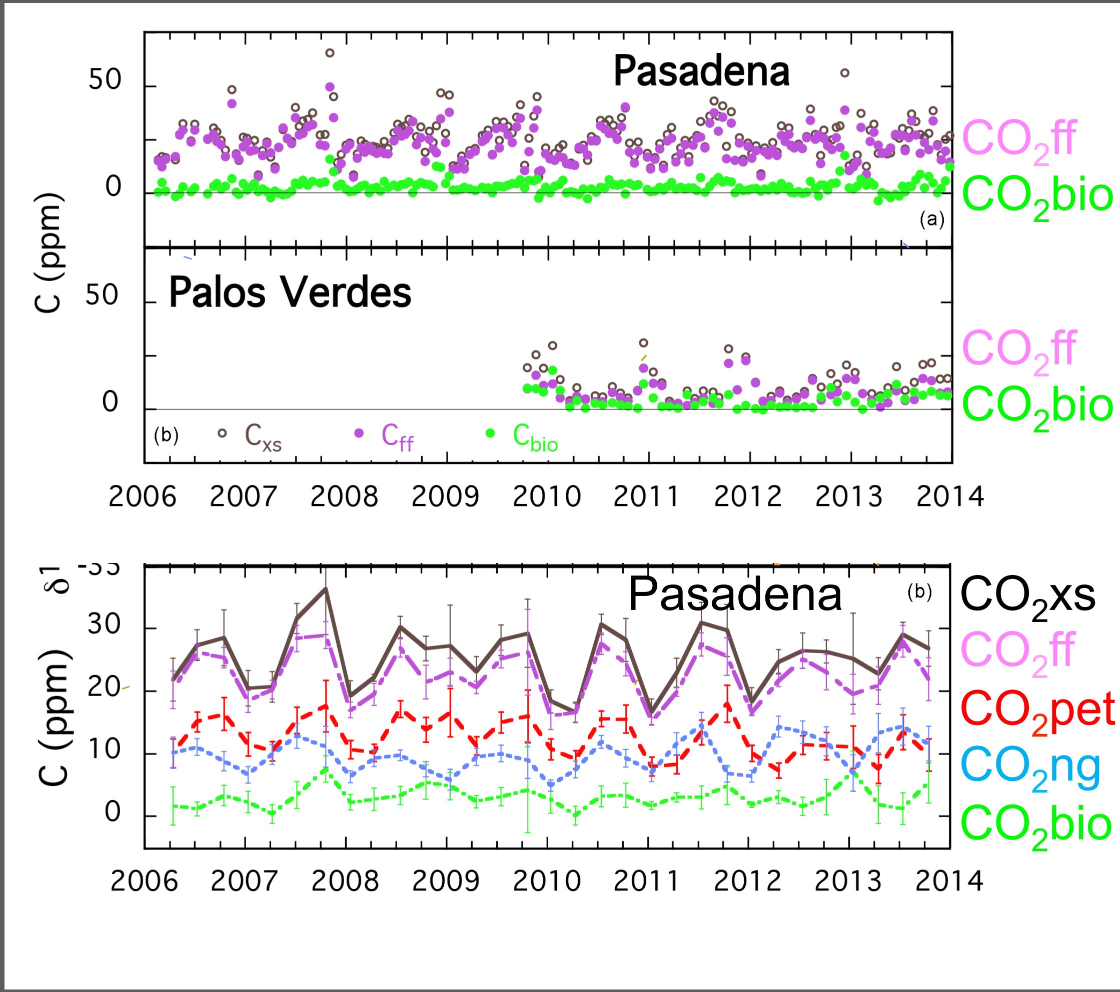






Partitioning by fossil fuel type with ^{13}C
Los Angeles, Newman et al 2016





Other tracers

- Hydrocarbons – often related to traffic sources
- Halocarbons – associated with particular processes/source sectors
- Reactive gases – short lifetime might help with identifying nearfield vs farfield GHG emissions
- COS, ^{18}O – separate biogenic processes

Conclusions

^{14}C is the gold standard for partitioning CO_2 into fossil and biogenic components

Correlate tracers such as CO can provide higher resolution CO_2ff – when CO:CO_2ff ratio is known

Can use same measurements to evaluate CO and other correlate tracer emission rates

Other trace gases (hydrocarbons, halocarbons, pollutants) may also be useful but are not yet well explored