Atmosphere-based estimates of non-CO_2 greenhouse gas emissions for the U.S. derived from $^{14}CO_2$.

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See related work in Poster by L. Hu

Abstract: The small radiocarbon fraction of atmospheric CO_2 (~1:10^{12} ^{14}C:C) has proven to be an ideal tracer for the fossil fuel derived component of observed CO_2 (C_{ff}) over large industrialized land areas. High-precision $^{14}CO_2$ measurements are being made in air sampled from a network of tall towers and airborne profiling sites around the U.S. together with measurements of more than 20 other anthropogenic trace gases including CO, CH_4, N_2O, SF_6, and halo- and hydro-carbons. Pairing C_{ff} with boundary-layer concentration enhancements of these gases allows us to determine apparent emissions ratios for each gas with respect to C_{ff}. When combined with model-derived spatial footprints and inventory-based fossil fuel emissions, absolute emission rates for the correlate gases can be derived, following simple scaling methods we have outlined previously [Miller *et al*. 2012, *J. Geophys. Res.,* doi:10.1029/2011JD017048]. Here we present emission magnitudes derived for select gases in regions of significant urban and industrial activity around the U.S. based on measurements in California, Texas, the mid-west, south-east and north-east. Statistically significant and coherent spatial and seasonal patterns in emissions ratios and absolute emissions are determined for many gases based on measurements over multiple years. We believe this approach provides reliable 'top down', observationally-based emissions estimates for these gases, many of which influence climate, air quality and stratospheric ozone.

Goal:

Derive atmosphere-based emission magnitudes for chemicals influencing climate, ozone, & air quality on a national scale.

Approach:

Emissions of a trace gas X_1 are derived by scaling measured covariations in atmospheric mole fraction by "known" emissions of trace gas X_2:

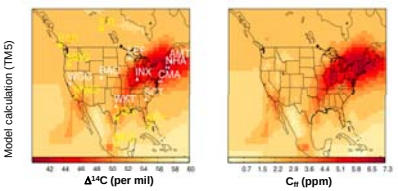
$$\text{Emissions}(X_1) = \Delta X_1 / \Delta X_2 \times \text{Emissions}(X_2)$$

where ΔX_n the concentration enhancements above background

and ΔX_2 is the fossil-fuel CO_2 (C_{ff}) concentration derived from measurements of $^{14}CO_2$

** **Emissions (C_{ff}) are known with high relative accuracy from the Vulcan fossil fuel inventory (Gurney *et al*., 2009)**

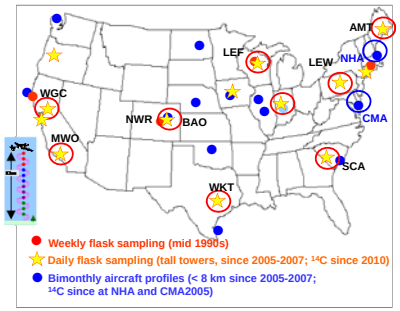
$\Delta^{14}CO_2$ is an excellent proxy for C_{ff}



* In a model, distribution of C_{ff} dominates the $\Delta^{14}CO_2$ signal over NH land area
→ nuclear power and respiration influences are small
→ figures here are scaled according to mass balance relation of –2.7‰/ppm CO_2

* In practice, measurement precision allows determination of C_{ff} within ±1 ppm
→ see Miller *et al*., 2012.

Tall tower and aircraft flask sampling network



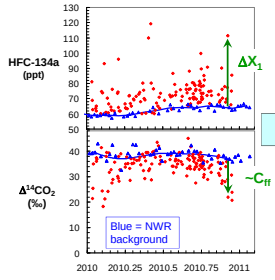
40-50 trace gases are measured in all flasks:

CO_2 $^{13}CO_2$ $^{14}CO_2$ $C^{18}OO$
CH_4 N_2O SF_6 CO
COS H_2
4 CFCs (-11, -12, -113, -115)
3 HCFCs (-22, -141b, -142b)
6 HFCs (-134a, -125, -143a, -152a, -365mfc, -227ea)
3 halons (-1211, -1301, -2402)
5 Hydrocarbons (C_2H_2, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_6)
3 methyl halides (CH_3Cl, CH_3Br, CH_3I)
Multiple chlorinated and brominated methanes and ethanes

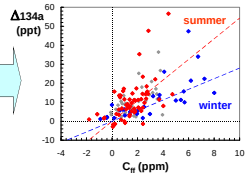
$^{14}CO_2$ is measured in a subset of flasks
from tower sites (red circled sites above)
from aircraft (blue circled sites; Miller *et al*., 2012)
and at Niwot Ridge, CO (NWR)
Results from LEF, LEW and AMT are **not** used in this analysis

Deriving ΔX_1 and C_{ff} from air sample measurements:

Example observations at WKT (red points) relative to background site (NWR blue points):



Apparent Emission Ratios (derived as the median observed mixing ratio enhancement)
HFC-134a *vs.* C_{ff} at WKT (2010)

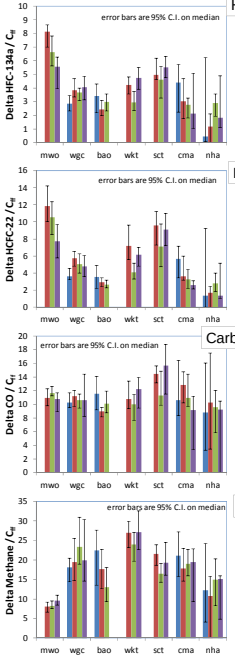


$C_{ff} = (\Delta^{14}C_{obs} - \Delta^{14}C_{bkgd}) / -2.7$ + respiration term*

Where 1 ppm C_{ff} (ppm) → –2.7‰

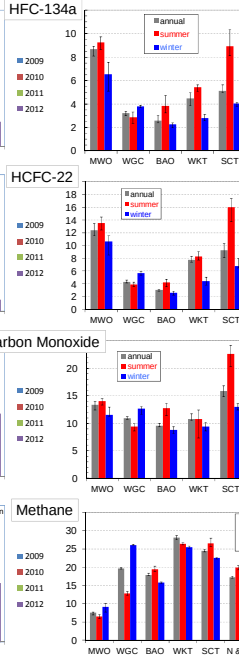
* the respiration term arises from respiration of "bomb CO_2" back to the atmosphere; its magnitude is likely < 0.8 ppm and is not yet explicitly estimated here

Enhancement Ratios by site and year



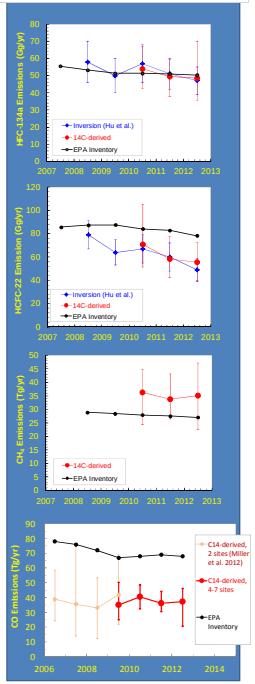
Large differences are observed in enhancement ratios at different sites. Interannual differences are typically smaller.
→ **Substantial biases are expected in total US emissions if derived from only a few sites.**

2010 Enhancement Ratios by site and season



Seasonal varying enhancement ratios are observed for the refrigerants (HFC-134a and HCFC-22), and for CO at some sites.
→ **Seasonality substantially influences estimates for some gases.**

U.S. emissions derived from $^{14}CO_2$

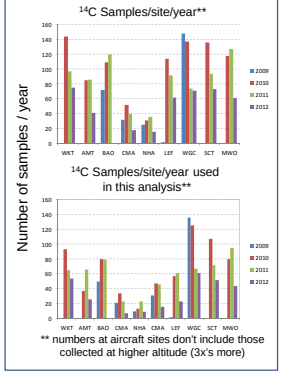


Emissions from our ^{14}C analysis (red points) compared to those from an independent inverse analysis of data obtained from this same sampling program—**See poster by L. Hu**–and U.S. EPA inventory estimates and, for CO, from ^{14}C data at NHA and CMA only (Miller *et al*., 2012)

Conclusions

* ***Advances in high precision ^{14}C measurements*** from small volume samples and the development of a U.S-wide ***automated flask sampling network*** are enabling nationally-representative emission estimates for a range of trace gases affecting climate, stratospheric ozone, & air quality over Time
* Fairly high correlations are observed between pollution-related concentration enhancements above background for many chemicals and fossil-fuel-derived CO_2.
* Measurements of ^{14}C and C_{ff} allow derived emissions to be tied to the fairly accurate US C_{ff} inventory.
* Observed enhancement ratios show substantial variations across regions and seasons that must be accounted when deriving accurate, top-down national emission magnitudes.
* *Derived emissions are very consistent with the inverse analysis of L. Hu (see other poster).*
* Results for HFC-134a are very consistent with the US EPA inventory-based result. Larger differences are noted for other gases.

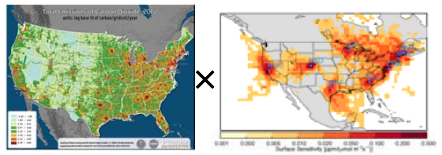
The decline in samples collected and analyzed for ^{14}C



** numbers at aircraft sites don't include those collected at higher altitude (3x's more)

Deriving site-specific C_{ff} emissions

Fossil-fuel emission inventory × **Site sensitivity to surface emissions**



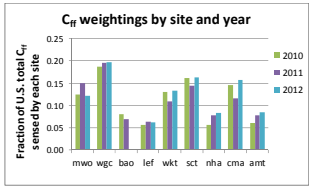
Gurney, K.R., *et al.* (2009); 2008 emissions.

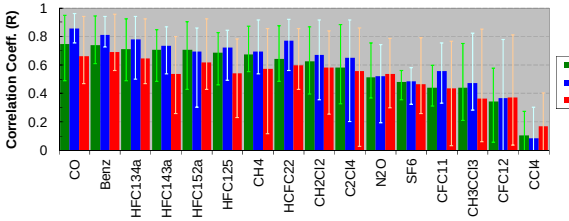
Footprint calculated with STILT Lagrangian trajectory model driven by WRF winds at 10 km resolution

Site-specific sensitivities to fossil emissions are derived from the Vulcan fossil-fuel emission inventory by convolving them with site-specific surface sensitivity footprints for collected samples.

Sensitivities are then normalized to the US total fossil fuel emission

C_{ff} weightings by site and year





Correlation coefficients for different trace gases averaged over 2010-2012 at all seven sites. The 'error bars' indicate the ***range*** in R among the seven sites.

Next steps:

* maintain the observational network; regain ^{14}C sampling frequency
* add robust estimates of respiration influences on derivation of C_{ff}
* improve background determination to include back-trajectory information and our measurements from remote regions

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References:
* Gurney, K.R. D.L. Mendoza, Y. Zhou, M.L. Fischer, C.C. Miller, S. Geethakumar, S. De La Rue Du Can, *Environ. Sci. Technol, 43*, 2009;43(14):5535-5541, doi:10.1021/es900806c, 2009.
* Miller, J.B., S.J. Lehman, S.A. Montzka, C. Sweeney, B.R. Miller, A. Karion, C. Wolak, E.J. Dlugokencky, J. Southon, J.C. Turnbull, P.P Tans, *JGR-A, 117*, D08302, doi:10.1029/2011JD017048, 2012.