^{14}C-based emission estimates for halocarbons and other greenhouse gases across the U.S.

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The problem:

- U.S. emissions of greenhouse gases and ozone-depleting substances are derived almost entirely from inventories.
- Inventories are based on many unchecked assumptions and can be grossly in error.
- GMD's capabilities allow us to independently estimate emissions on continental scales.

Our approach:

- Measure co-variations between trace gases and $^{14}CO_2$ in polluted air at selected North-American sites.
- Use $^{14}CO_2$ to derive the recent fossil-fuel contribution in each sample.
- Derive trace gas emissions from the observed co-variations and inventory-based U.S. fossil-fuel emissions.

General approach for estimating regional emissions:

Emissions(X_1) = $\Delta X_1 / \Delta X_2 \times$ Emissions(X_2)

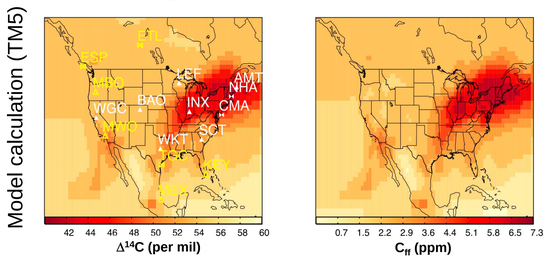
ΔX_1 = concentration enhancement above background for trace gas X_1

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

Emissions(X_2) = C_{ff}, are known with high relative accuracy from the Vulcan fossil fuel inventory (Gurney *et al*., 2009)

Methodology background:

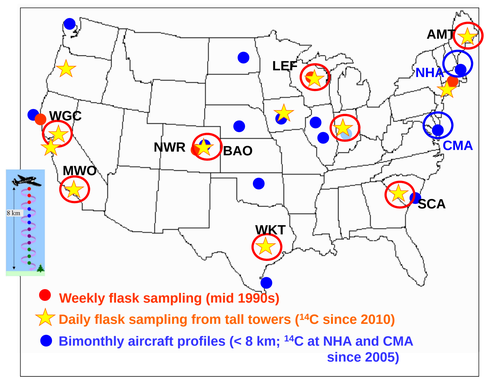
$\Delta^{14}CO_2$ is an excellent proxy for C_{ff}



* Across North America the distribution of C_{ff} dominates the $\Delta^{14}CO_2$ signal
→ 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.

1) Tall tower & aircraft sampling network



40-50 trace gases are measured in all flasks:

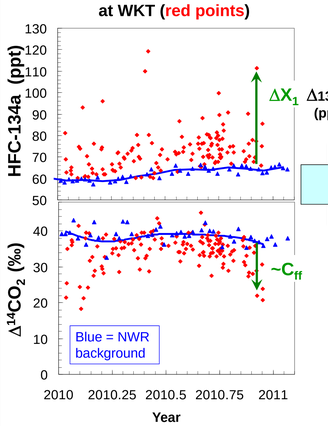
CO_2	$^{13}CO_2$	$C^{18}OO$	CH_4	N_2O	SF_6
CO	COS	H_2			

4 CFCs — 3 HCFCs
6 HFCs — 3 halons
5 Hydrocarbons — 3 methyl halides
Multiple chlorinated and brominated alkanes

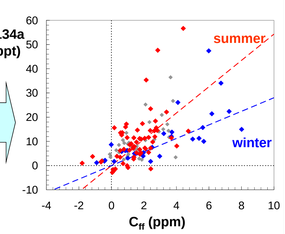
$^{14}CO_2$ measured in a subset of flasks in 2010:
at tower sites: red circles
aircraft profiles: blue circles
& Niwot Ridge, CO (NWR)

2) Deriving ΔX_1 and C_{ff} from air sample measurements during 2010:

Example observations at WKT (red points)



Mixing Ratio Enhancements 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‰

* from respiration of "bomb CO_2" back to the atmosphere (typically < 0.8 ppm)

3) Apparent Emission Ratios $\Delta X / C_{ff}$ measured at sites across the U.S.

Average r^2 during summer and winter

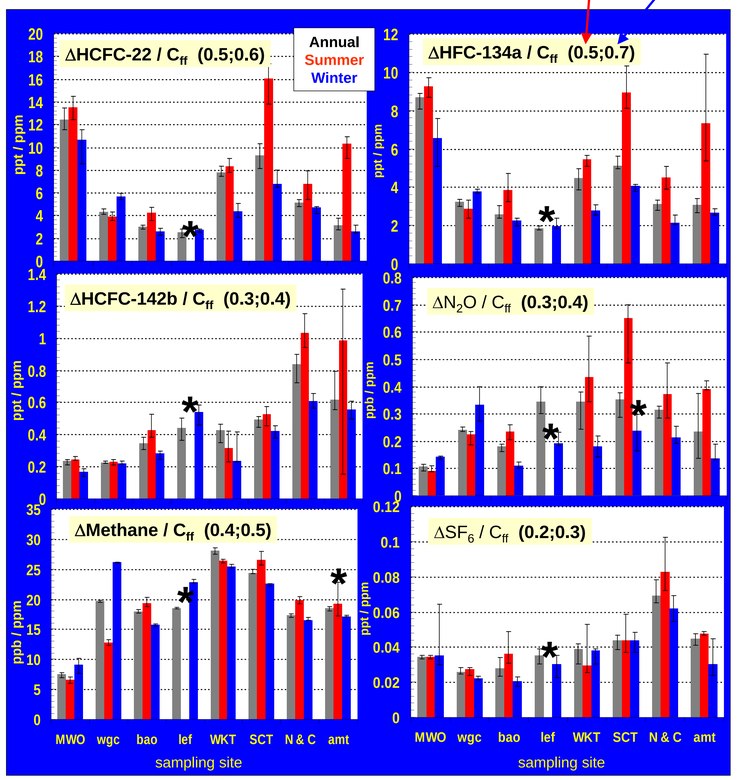


Figure Key:
Observed annual and seasonal apparent emission ratios at each of 7 tower and two aircraft sites during 2010 from median enhancements:
All year (grey); Summer (red); Winter (blue)

Results:

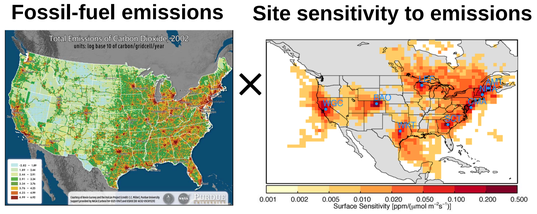
Apparent emission ratios (ΔX *vs.* C_{ff}) vary by region and season in ways that are intuitively reasonable. For example:

Ratios to C_{ff} in the UPPER panel show:
* Refrigerant fluids (HCFC-22 and HFC-134a) show expected seasonality.
* Insulation foam blowing agent (HCFC-142b) is enhanced at northerly sites.

Ratios to C_{ff} in the LOWER panel show:
* Methane shows a rather unique pattern.
* SF_6 is highest in the North-Eastern U.S.

4a) Site-specific C_{ff} emissions are derived from convolving:

Fossil-fuel emissions × **Site sensitivity to emissions**

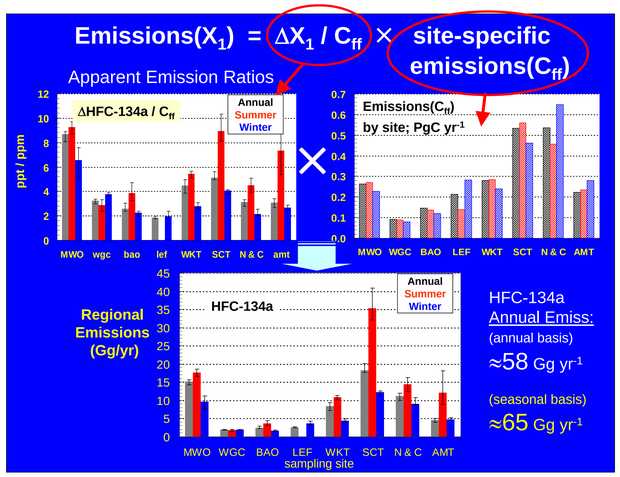


Inventory from Gurney, K.R., *et al*. (2009)

STILT Lagrangian trajectory model and WRF winds (10 km res)

4b) Site-specific emissions derived for HFC-134a for 2010:

Emissions(X_1) = $\Delta X_1 / C_{ff} \times$ site-specific emissions(C_{ff})



→ Covariations in apparent emission ratios and C_{ff} can cause substantial errors if the calculation is done on an annual basis (*e.g.*, 58 vs 65 Gg/yr for HFC-134a here)

Annual national emissions (preliminary estimates):

Chemical		Miller *et al.** 2006-2009	this work** 2010	EPA * 2005-2009	EDGAR * 2005-2009	this work CO_2-eq (GtC)
CO	Tg yr^{-1}	41 (16-73)	48	77	62	--
SF_6	Gg yr^{-1}	1.4 (0.7-3.0)	0.9	0.7	1.8	0.006
HFC-134a	"	46 (10-86)	65	55	70	0.024
HCFC-22	"	66 (19-138)	87	85	--	0.042
CH_4	Tg yr^{-1}	39 (18-69)	41	32	26	0.280
N_2O	Tg yr^{-1}	1.7 (0.7-3.6)	1.8	1.0	1.0	0.146
Region/ # of sites>>		cma&nha	nine	All US	All US	sum>> 0.50

* As reported in Miller *et al*. (2012), from aircraft sites NHA & CMA (N&C) only.
***** Scaled to total US C_{ff} emission of 1.6 PgC yr^{-1}***

Conclusions

From atmospheric measurements of chemicals affecting climate, ozone, and air quality at nine U.S. sites during 2010 ***and*** $^{14}CO_2$:

* **Fairly high correlations are observed** between pollution-related concentration enhancements above background for these chemicals and fossil-fuel CO_2.
* **Emissions on regional and national scales are derived** based on these co-variations with consideration of the US C_{ff} inventory.
* **Regional emissions show substantial variations across regions and seasons** that need characterization for an accurate evaluation of inventory estimates.

Next steps:

* maintain & expand observational network to improve coverage
* continue to improve methodology by:
- refining respiration influences on C_{ff} estimation
- improving background determination
- defining robust uncertainties

* assess our new methodology by comparing with other techniques (*e.g.*, correlations to CO; regional modeling approaches using the broader suite of available data.

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