## Observational constraints on U.S. emissions of halocarbons from multiple NOAA sampling networks

<u>S. Montzka</u><sup>1</sup>, B. Miller<sup>1,2</sup>, C. Siso<sup>1,2</sup>, C. Sweeney<sup>1,2</sup>, A. Andrews<sup>1</sup>, A. Karion<sup>1,2</sup>, D. Neff<sup>1</sup>, M. Fischer<sup>3</sup>, J. Higgs<sup>4</sup>, B. Hall<sup>1</sup>, J.W. Elkins<sup>1</sup>, P. Tans<sup>1</sup>. <sup>1</sup>NOAA / Earth System Research Laboratory <sup>2</sup>CIRES, Univ. of Colorado <sup>3</sup>Lawrence Berkeley National Laboratory <sup>4</sup>Science Technology Corp.

Thanks to L. Miller, J. Kofler, S. Wolter, K. Masarie, and others D. Godwin (EPA), Sample collectors, pilots

M. Trainer (CSD), D. Blake (UCI), E. Atlas (Univ. of Miami)

Goal: use atmospheric data to assess greenhouse gas emissions and their change over time...

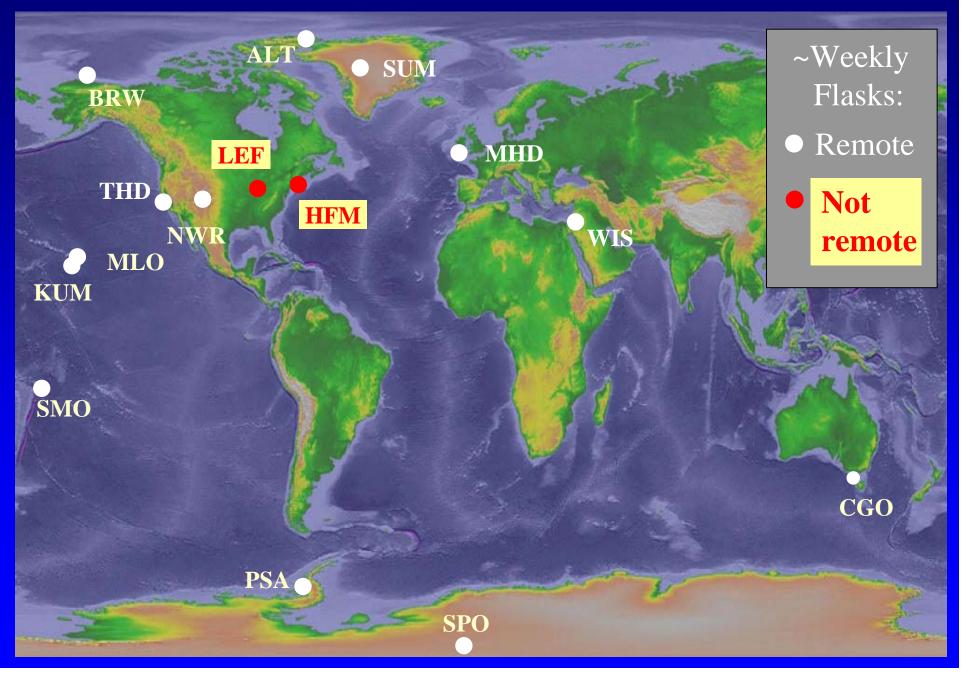
For today, a progress report on emission signals in data

- Mixing ratio enhancements in the US continental boundary layer

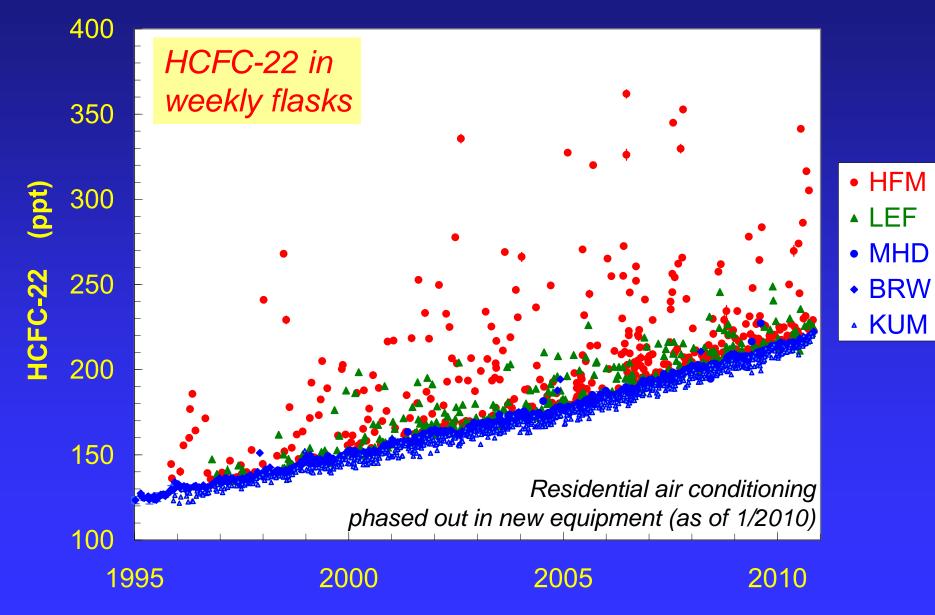
→ HFC-134a vs. HCFC-22

- correlated enhancements
- the results suggest emissions that vary over time, space, and season

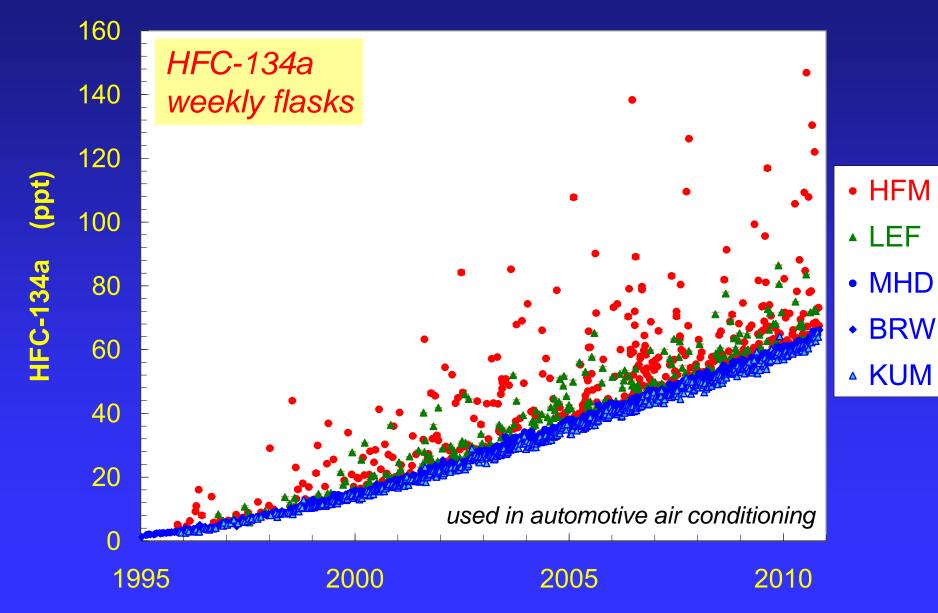
## **NOAA's Cooperative Global Sampling Network**



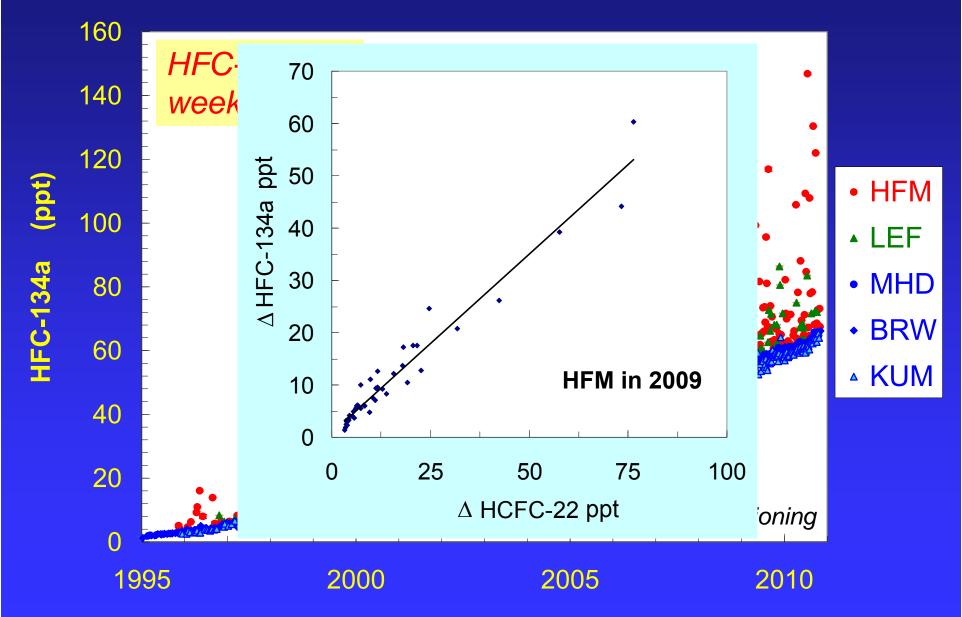
# Mixing ratios at mid-western and eastern continental U.S. sites are enhanced above background



# Mixing ratios at mid-western and eastern continental U.S. sites are enhanced above background



# Mixing ratios at mid-western and eastern continental U.S. sites are enhanced above background



#### Enhancements are correlated and change over time Annual mean correlation slopes from measured enhancements

HFM ~ weekly 1.0 LEF ~ weekly  $\Delta$  HFC-134a /  $\Delta$  HCFC-22 **0.8** 0.6 0.4 0.2 0.0 2002 1992 1997 2007 Results from both sites suggest increasing emissions of HFC-134a relative to HCFC-22 over time...

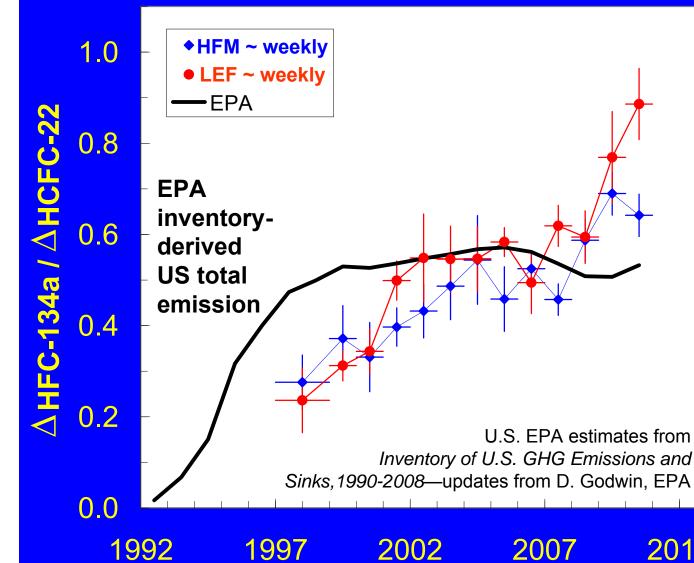
<u>Average annual  $r^2$ :</u> HFM: 0.9  $\pm$  0.04 LEF: 0.9  $\pm$  0.05 n = 30 to 40 /yr

Year

ODR slopes

2012

#### **Correlated enhancements compared to US emissions** Annual mean correlation slopes from measured enhancements

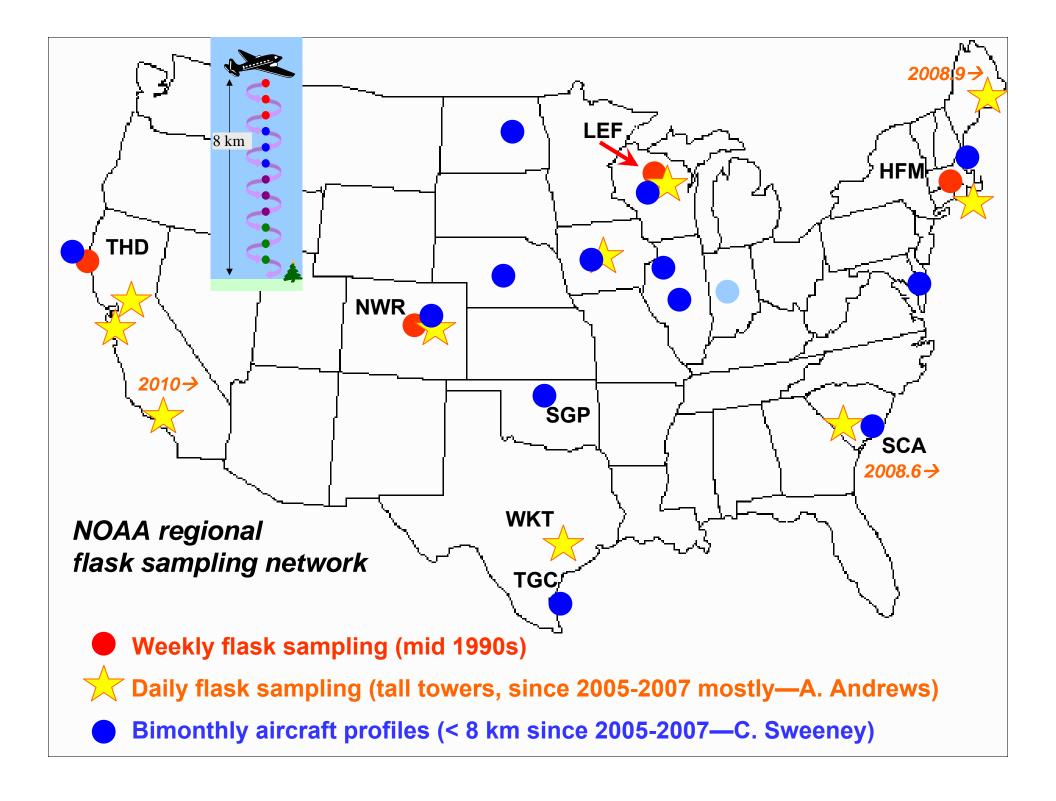


Do enhancements provide information about total US emissions?

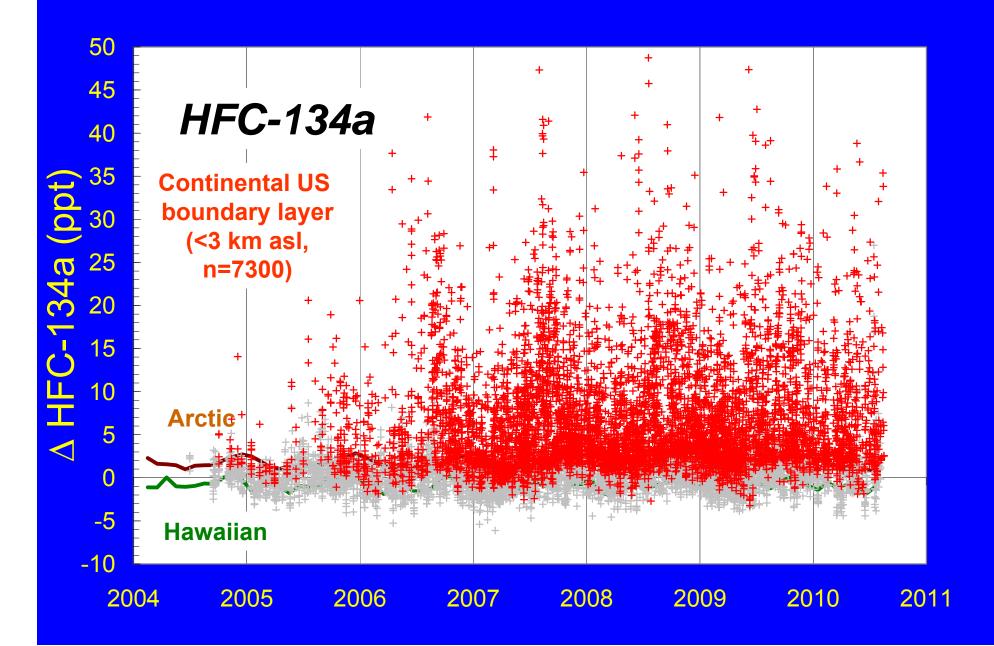
How accurate and representative are these results (two sites & 30-40 samples/yr)?

2012

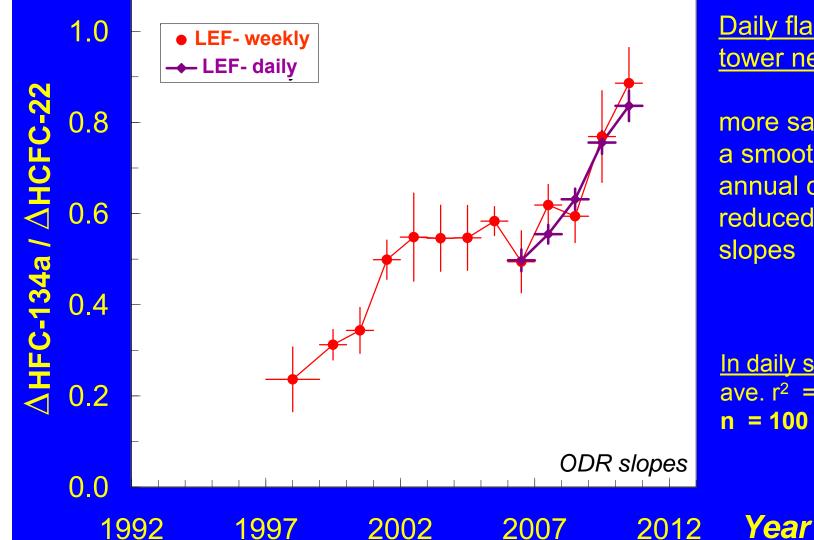
Year



#### Additional data from pfp sampling program



#### Enhancements are correlated and change over time Additional samples add robustness to slopes

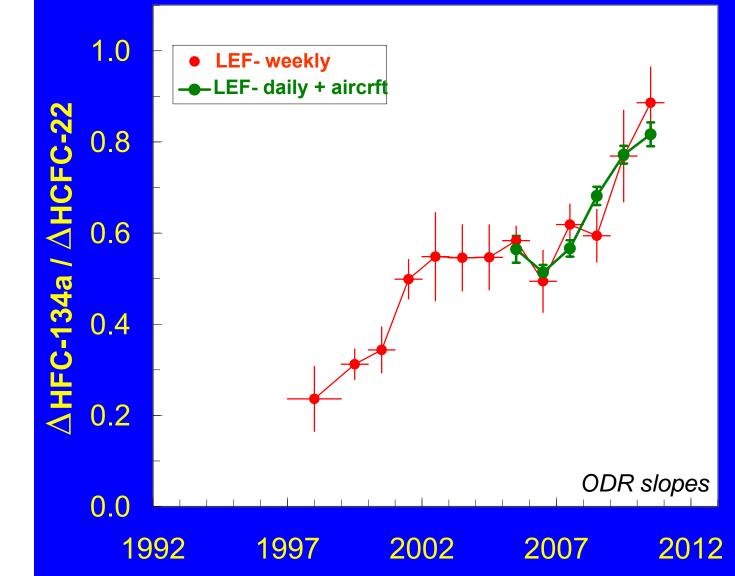


Daily flasks from tower network:

more samples yield a smoother interannual change and reduced error in slopes

In daily samples: ave.  $r^2 = 0.9 \pm 0.02$ n = 100 to 370 /yr

#### Enhancements are correlated and change over time Additional samples add robustness to slopes

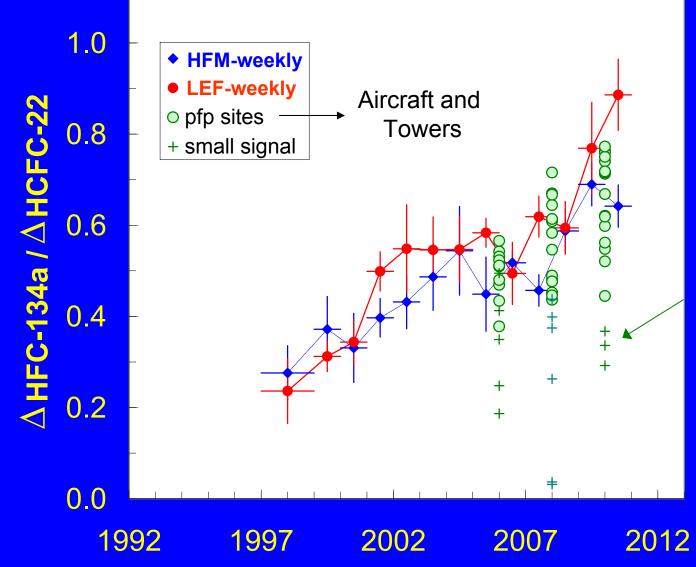


Adding results from aircraft (< 3 km) reduces error additionally...

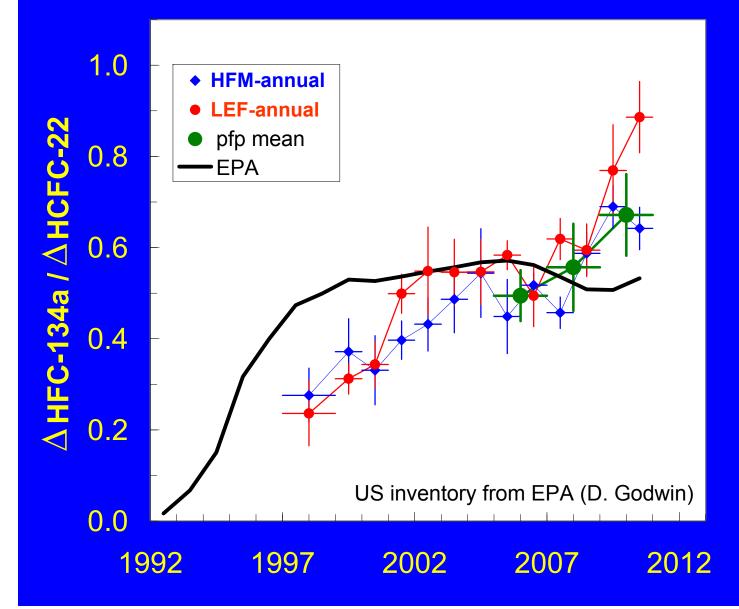
Including aircraft data likely makes this result representative of a broader region

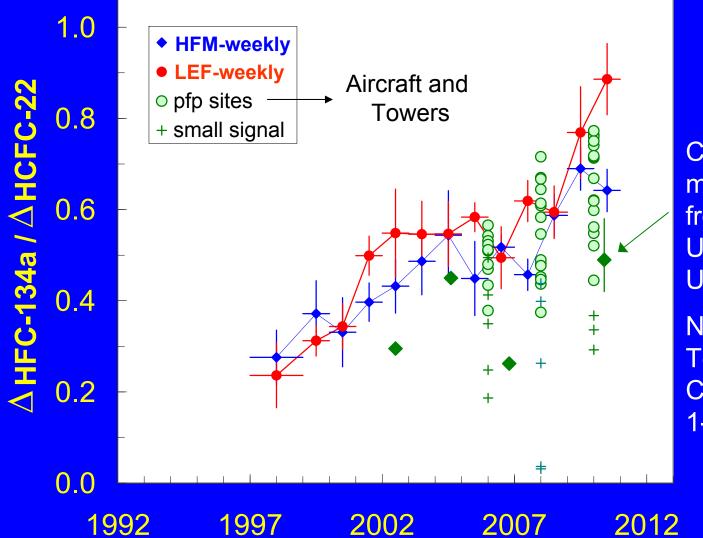
<u>In these results</u> Ave annual r<sup>2</sup> = 0.93 ± 0.02 n = 140 to 740 /yr

Year



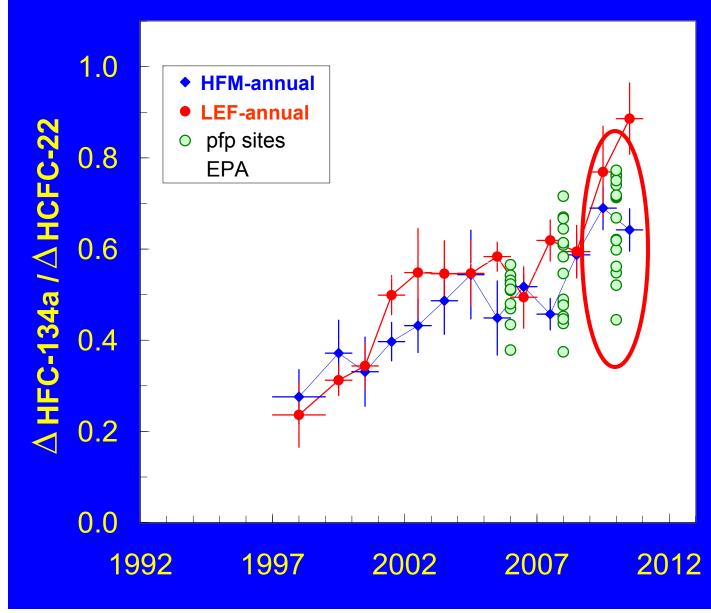
"small signal" sites have small mean enhancements or  $r^2 < 0.6$ 





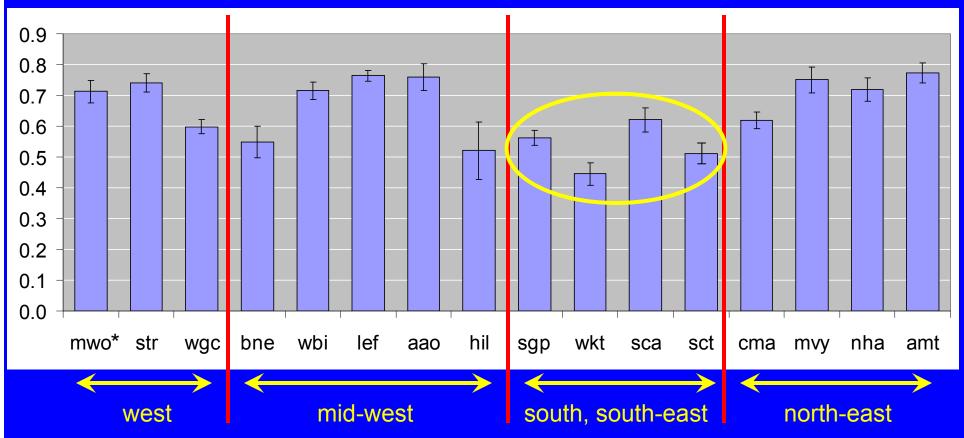
CSD/NOAA aircraft missions (Flask data from D. Blake @ UCI and E. Atlas @ Univ. of Miami)

NEAQS TexAQS CalNEX 1-2 month duration



What does this variability represent??

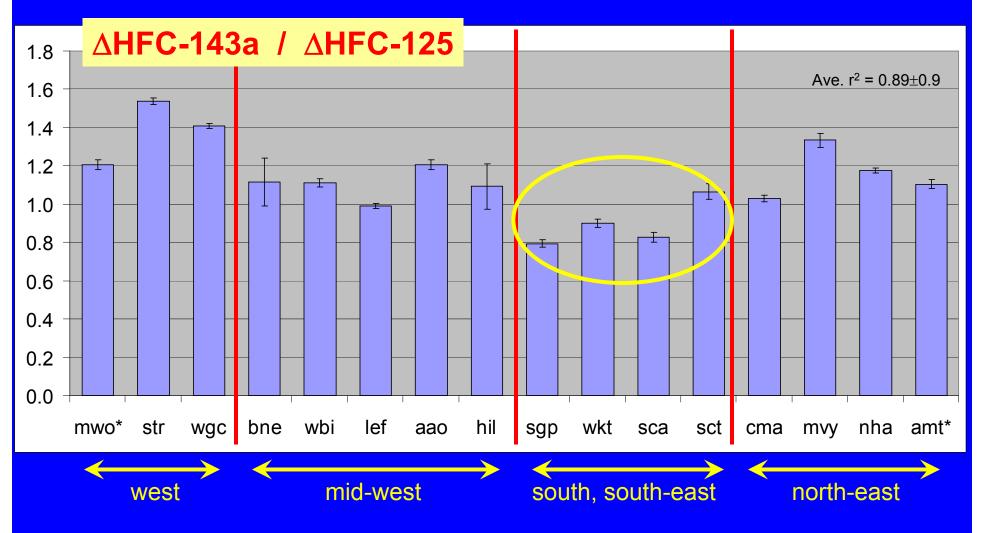
### $\triangle$ HFC-134a / $\triangle$ HCFC-22—at different sites, 2009-2010



#### HFC-134a → mobile AC HCFC-22 $\rightarrow$ residential AC

While all autos have AC (HFC-134a), not all houses do (HCFC-22).  $\rightarrow$ Ratio is sensitive to residential AC penetration, which is higher in the southern US states...

### Enhancement ratios at multiple sites -- 2009-2010



HFC-125 is a replacement for HCFC-22 in residential AC —its use is also likely higher in the South

# **Conclusion:**

→A "data only" analysis of results from a national-scale sampling network suggests:

Weekly samples can provide useful information...
but additional samples add robustness

<u>U.S. emissions of HFC-134a are increasing relative</u>
<u>to HCFC-22...</u>

- and recent increases are not captured by inventories

<u>Regional variations in emission patterns were observed...</u>
*Sampling at more sites gives better information*

<u>Seasonal variations in emissions are observed (not shown)</u>
*only year-round programs can provide an annual mean*