Carbon tetrachloride (CCl_4) emissions from the US during 2008 – 2012

L. Hu[1,2], S. A. Montzka[2], B. R. Miller[1,2], A. E. Andrews[2], J. B. Miller[1,2], S. Lehman[3], C. Sweeney[1,2], D. Godwin[4], K. Thoning[2], H. Chen[5], M. L. Fischer[6], C. Siso[1,2], E. Atlas[7], D. Blake[8], J. A. de Gouw[1,9], J. B. Gilman[1,9], W. C. Kuster[1,9], J. W. Elkins[2], B. D. Hall[2], and P. Tans[2]

1. Cooperative Institute for Research in Environmental Sciences, University of Colorado-Boulder, Boulder, CO, USA; 2. NOAA Earth System Research Laboratory, Global Monitoring Division, Boulder, CO, USA; 3. Institute of Arctic and Alpine Research, University of Colorado-Boulder, Boulder, CO, USA; 4. US Environmental Protection Agency, Washington DC, USA; 5. Centre for Isotope Research, University of Groningen, Groningen, The Netherlands; 6. Environmental Energy Technologies Division, Lawrence Gerkeley National Laboratory, Berkeley, CA, USA.; 7. Rosenstiel School of Marine & Atmospheric Science, University of Miami, FL, USA; 8. School of Physical Sciences, University of California – Irvine, CA, USA; 9. NOAA Earth System Research Laboratory, Chemical Science Division, Boulder, CO, USA;

Correspondence to: lei.hu@noaa.gov

Motivation

- **Importance of CCl_4**
  - It depletes stratospheric ozone (ODP = 0.82)
  - It is a potent greenhouse gas ($GWP_{100year}$ = 1730)
- **CCl_4 mystery**

  - Global production and consumption of CCl_4 for emissive uses have been phased-out for many years due to the Montreal Protocol (MP). However, emissions derived from reported production and feedstock uses of CCl_4 are much less than those derived from atmospheric observations (in 2012, the difference is ~30 – 80 Gg/y).
- **US CCl_4 emission**
  - Inventory-based emission reported by US EPA: < 0.5 Gg/y from 1996 to the present.
  - Atmosphere-derived emissions:

    Hurst et al (2006): not detectable (based on aircraft campaigns and correlation with CO)

    Millet et al (2009): not detectable (based on aircraft campaigns and correlation with CO)

    Miller et al (2012): 0.4 (-5.6 – 14) Gg/y (based on two long-term aircraft sites in the northeast of the US and correlation with $^{14}CO_2$)
- **Questions to be addressed**

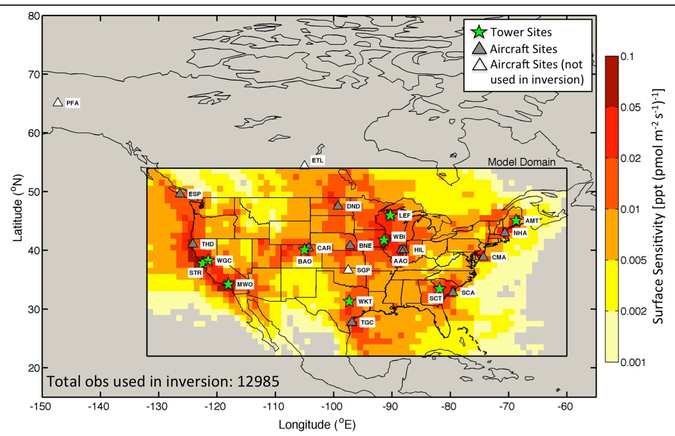
  - Are US CCl_4 emissions really close to zero? Or were the previous atmosphere-based studies not conducted during emissive times or over emissive regions? Or were there other reasons (e.g. poor measurement precision, poor correlation with their selected tracers) that limited their ability to estimate CCl_4 emissions?

  - With our extensive long-term air sampling network over the US and high-precision measurements we made, what emission magnitudes of CCl_4 are implied?

  - If US CCl_4 emissions are above zero, where do those emissions come from?

  - Based on our atmospheric observations, can we identify any possible sources of CCl_4 that contribute to its on-going global emission?

CCl_4 measurements over North America from NOAA GMD's Greenhouse Gas Reference Network



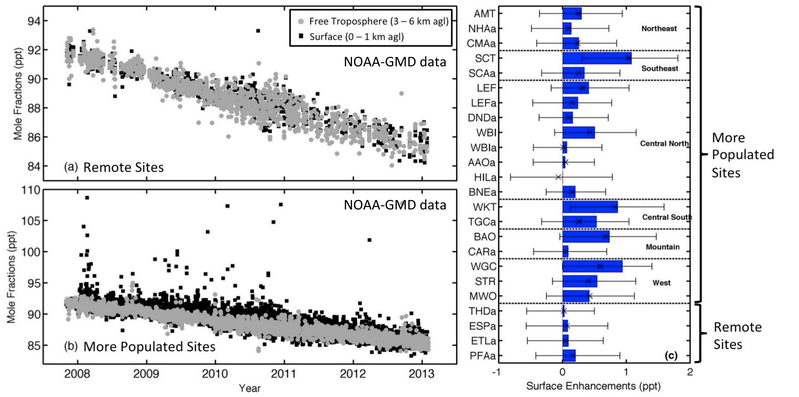
- We are in the best position to provide the most reliable atmosphere-derived US emission of CCl_4 because:

  - We have the most extensive long-term monitoring air-sampling network over the US (9 tower sites and 12 aircraft sites).

  - 100% of grid cells over the contiguous US have an average sensitivity above 0.002 ppt (pmol m^{-2} s^{-1})$^{-1}$ and 80% is above 0.005 ppt (pmol m^{-2} s^{-1})$^{-1}$

Acknowledgements:
Thanks to K. Masarie for discussion of calculating background, R. Draxler and A. Stein for assistance with running HYSPLIT footprints, D. Mondeel, J. Higgs, M. Crotwell, P. Lang, W. Wolter, D. Neff, J. Kofler, and others involved with sampling, analysis, logistics, and program management, and S. Biraud and M. Torn for sampling at SGP.

Observational Evidence for Surface Emissions of CCl_4 within the US



- **Remote sites** (upper left panel): comparable mole fractions of CCl_4 between the surface (<1 km agl) and free troposphere (3 – 6 km agl) suggest no vertical gradient of CCl_4 in background atmosphere between 20 – 70 °N and no significant influence of loss processes (i.e. soil or ocean uptake, stratospheric photolysis) on the vertical gradient in the lower troposphere (<6km).
- **More populated sites** (lower left panel): Enhanced mole fractions at the surface relative to free tropospheric data suggest enhancements related to surface emissions.
- **Spatial distribution of enhancements** (right panel): Larger enhancements at sites around SCT, WKT, TGC, BAO, WGC and STR, suggest possibly larger emissions over those regions.

US national- and regional- emissions of CCl_4

Method: Bayesian inversion

Basis of Bayesian inversion:

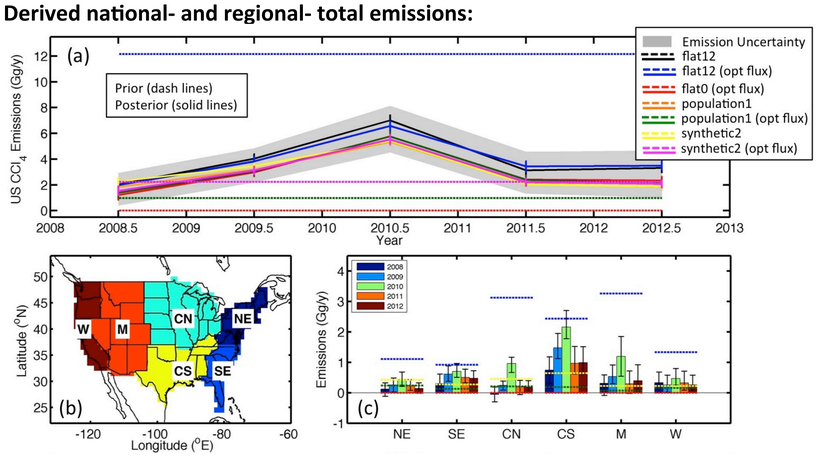
Observed enhancements = Fluxes X Footprint (sensitivity of observed enhancements to upstream fluxes) + Model-data mismatch errors

Computed using HYSPLIT- NAM12

Estimated using maximum likelihood estimation

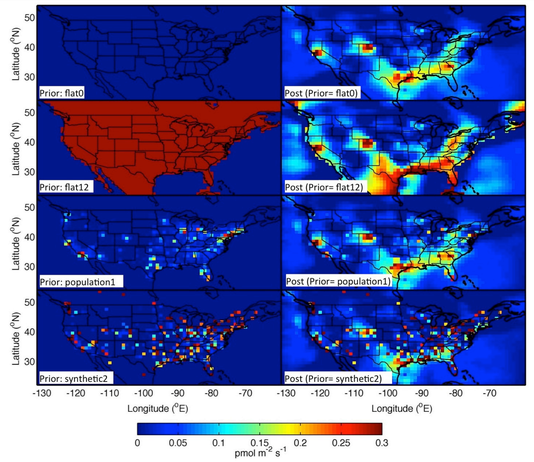
Solve for: monthly 1° × 1° fluxes or scaling factors for a prior flux field

Derived national- and regional- total emissions:



- Derived US national total emissions of CCl_4 (averaged over 2008 – 2012), 2.6 – 4.2 Gg/y, are 5 to 8 times the upper limit of US EPA reported emissions.
- Derived national total emission in 2010 is 2 – 3 times that in other years. This variability is robust during 2010 – 2012 and less so during 2008 and 2009 due to lack of observations at AMT and SCT in 2008 and at MWO for both years.
- Distributions of regional total emissions are consistent across results derived from different priors. They indicate 30 – 50% of national emissions are from the central south of the US.

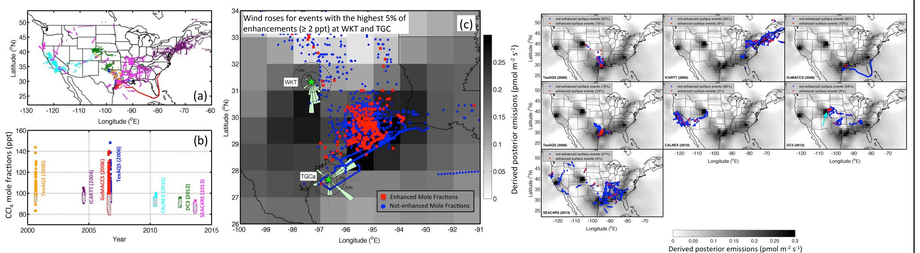
Emission hotspots of CCl_4



- Spatial distribution of the posterior emission [derived from a flat prior (flat0)] that is purely driven by atmospheric observations show four emission hotspots.
- At these four emission hotspots, derived emissions from other priors are consistently shown enhanced although derived grid-scale emissions are dependent on prior emissions.

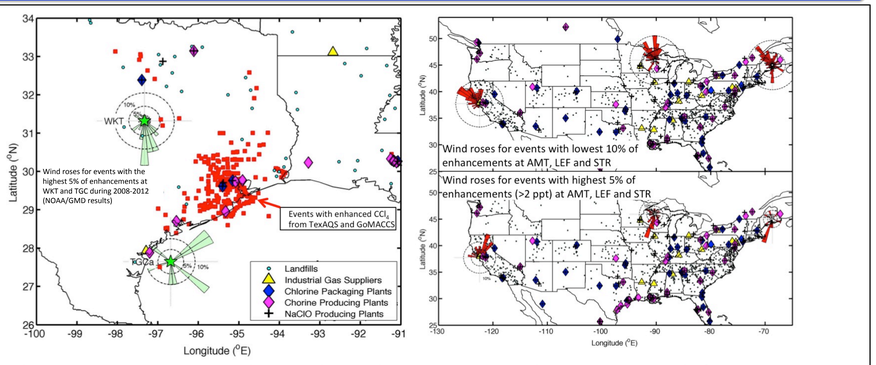
Note: The prior of "synthetic2" was created based on distributions of possible sources of CCl_4 (i.e. chlor-alkali plants, industrial gas producers, and landfills) suggested by previous studies.

Additional independent evidence supporting derived emission hotspots of CCl_4 [measurements from NOAA/CSD (J. de Gouw, J. Bilman, and W. Kuster), University of Miami (E. Atlas) and University of California-Irvine (D. Blake)]:



- Substantial enhancements of CCl_4 observed during TexAQS (2000 and 2006) and GoMACCS (2006) campaigns were located at Houston, Texas area where we derive enhanced emissions (gray shading). Moreover, air in which CCl_4 enhancements were ≥2 ppt at WKT and TGC mostly came from the same location.
- During DC3, enhanced mole fractions of CCl_4 are mostly concentrated around Denver, Colorado where we also derived enhanced emissions.

What are the possible sources that contribute to the ongoing emissions of CCl_4?



- Wind roses at AMT, STR, LEF indicate, when enhancements were low, air was mostly from remote area; when enhancements were high, air was mostly from more populated area where there are also proposed sources of CCl_4 (e.g. chlor-alkali plants, industrial gas suppliers and landfills).
- In Houston, Texas where enhanced emissions were derived and substantial enhancements were observed, there are a few collocated chlor-alkali plants, indicating they likely contribute to the CCl_4 emissions around this area.