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


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NOAA’s Climate Program Office and its Atmospheric Chemistry, Carbon Cycle, and Climate Program.

An extension of the analysis in:
Goal:
Derive atmosphere-based estimates of national emission magnitudes for chemicals influencing climate, ozone, & air quality.

Approach:
use multiple techniques…

For Today:

\[
\text{Emissions}(X_1) = \left[ \Delta X_1 / \Delta X_2 \right] \times \text{Emissions}(X_2)
\]

where:
* \( \Delta X_2 \) = fossil-fuel CO\(_2\) (C\(_{ff}\)) derived from measurements of \(^{14}\)CO\(_2\)
* \( \text{Emissions}(X_2) \) = fossil fuel emissions from the VULCAN inventory (Gurney et al., 2009)
\( \Delta^{14} CO_2 \) is a useful 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 \(-2.7\%_{oo}/ppm\)

* In practice, measurement precision allows determination of \( C_{ff} \) within \( \pm 1 \) ppm
Deriving $\Delta X_1$ and $C_{ff}$ from air sample measurements

**Apparent Emission Ratio**
(as median of point-by-point enhancements)

HFC-134a vs. $C_{ff}$ at WKT (2010)

**Observations at WKT (Texas)**
relative to background site

- HFC-134a (ppt)
- $\Delta X_1$
- $\sim C_{ff}$
- $\Delta ^{14}C_{CO_2}$

Blue = NWR background

$C_{ff} \approx (\Delta ^{14}C_{obs} - \Delta ^{14}C_{bkgd}) / -2.7 \% / ppm + \ldots$
40-50 trace gases are measured in flasks:

- CO$_2$
- $^{13}$CO$_2$
- $^{14}$CO$_2$
- C$^{18}$OO
- CH$_4$
- N$_2$O
- SF$_6$
- CO
- CFCs
- HCFCs
- COS
- H$_2$
- hydrocarbons
- methyl halides
- chlorinated and brominated methanes and ethanes

**NOAA regional flask sampling network**

- Weekly flask sampling (mid 1990s)
Apparent Emission Ratios ($\Delta X_1 / C_{ff}$):

- $\Delta CO / C_{ff}$ (0.4;0.7)
- $\Delta HFC-134a / C_{ff}$ (0.5;0.7)
- $\Delta HCFC-142b / C_{ff}$ (0.3;0.4)
- $\Delta HFC-152a / C_{ff}$ (0.4;0.6)

Annual:
- MWO
- wgc
- bao
- lef
- WKT
- SCT
- N & C
- amt

Summer:
- MWO
- wgc
- bao
- lef
- WKT
- SCT
- N & C
- amt

Winter:
- MWO
- wgc
- bao
- lef
- WKT
- SCT
- N & C
- amt
Deriving absolute emission rates:

\[
\text{Emissions}(X_1) = \left[ \frac{\Delta X_1}{C_{ff}} \right] \times \text{Emissions}(C_{ff})
\]

\[
\Delta \text{HFC-134a} / C_{ff}
\]

\[
\text{Annual}
\]

\[
\text{Summer}
\]

\[
\text{Winter}
\]

Emissions (HFC-134a) \approx 43 \text{ Gg yr}^{-1}

from NHA & CMA alone \approx 46 \text{ Gg yr}^{-1}

(Miller et al., 2012)
Emissions\( (X_1) \) = \( [\Delta X_1 / C_{ff}] \times \) Emissions\( (C_{ff}) \)

**Regional Emissions (Gg/yr)**

**HFC-134a**
- **Annual Emiss:**
  - (annual basis) \( \approx 58 \) Gg yr\(^{-1} \)
  - (seasonal basis) \( \approx 65 \) Gg yr\(^{-1} \)

**Emissions\( (C_{ff}) \)**
- by site and season
  - **Site-specific**
  - **C\(_{ff}\) emissions**

**Annual**
- **Summer**
- **Winter**

**\( \Delta HFC-134a / C_{ff} \)**
- **Annual**
- **Summer**
- **Winter**
Annual national emissions:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Miller et al.*</th>
<th>this work**</th>
<th>EPA *</th>
<th>EDGAR *</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>41 (16-73)</td>
<td>48</td>
<td>77</td>
<td>62</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>46 (10-86)</td>
<td>65</td>
<td>55</td>
<td>70</td>
</tr>
</tbody>
</table>

* As reported in Miller et al. (2012) from CMA & NHA only

** Scaled to total US C\(_f\) emission of 1.6 PgC yr\(^{-1}\)

For California:

<table>
<thead>
<tr>
<th></th>
<th>this work</th>
<th>CARB estimate for 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Tg yr(^{-1})</td>
<td>3.4</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>Gg yr(^{-1})</td>
<td>6.9</td>
</tr>
</tbody>
</table>

…from ave \(\Delta X_1/C_f\) at WGC and MWO in 2010 and Vulcan C\(_f\) for CA in 2002 scaled by EIA to 2010.
Refinements planned for the future:

1) Improving our estimates of:
   * background concentrations
   * emission ratios
   * surface sensitivity (footprints)

2) Adding observations at new sites to improve spatial coverage.

3) Performing inverse modeling analyses of all measurements.
   → with verification potentially provided by $^{14}$C.

4) Provide estimates of inter-annual emission changes.
Conclusions

From atmospheric measurements of a suite of chemicals affecting climate, ozone, and air quality at nine US sites during 2010:

* **State-wide and national scale emissions were derived**
  (based on measured atmospheric co-variations with fossil-fuel CO$_2$ and the VULCAN C$_f$ inventory)

* **Substantial variations noted across seasons and space**
  (necessary to characterize for deriving accurate and representative, top-down national emission magnitudes)

* Future work will focus on maintaining the observational network; refining our approach, defining robust uncertainties, and comparing results among multiple techniques.
Deriving site-specific $C_{ff}$ emissions

Fossil-fuel emission inventory

Site sensitivity to surface emissions


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

Site-specific $C_{ff}$ emissions can be derived by convolving the Vulcan fossil-fuel emission inventory with site- and season-specific surface sensitivity footprints.
Apparent Emission Ratios ($\Delta X_1 / C_{ff}$):

- **$\Delta$HCFC-22 / $C_{ff}$ (0.5;0.6)**
- **$\Delta$HFC-134a / $C_{ff}$ (0.5;0.7)**
- **$\Delta$HCFC-142b / $C_{ff}$ (0.3;0.4)**
- **$\Delta$HFC-152a / $C_{ff}$ (0.4;0.6)**
Apparent Emission Ratios ($\Delta X_1 / C_{ff}$):

- $\Delta CO / C_{ff}$ (0.4; 0.7)
- $\Delta Methane / C_{ff}$ (0.4; 0.5)
- $\Delta SF_6 / C_{ff}$ (0.2; 0.3)

Graphs showing annual, summer, and winter emissions for different regions (west, mid-west, north east) with error bars.
## Annual national emissions:

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<td>41 (16-73)</td>
<td>48</td>
<td>77</td>
<td>62</td>
</tr>
<tr>
<td>SF₆</td>
<td>1.4 (0.7-3.0)</td>
<td>0.9</td>
<td>0.7</td>
<td>1.8</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>46 (10-86)</td>
<td>65</td>
<td>55</td>
<td>70</td>
</tr>
<tr>
<td>CH₄</td>
<td>39 (18-69)</td>
<td>41</td>
<td>32</td>
<td>26</td>
</tr>
<tr>
<td>N₂O</td>
<td>1.7 (0.7-3.6)</td>
<td>1.8</td>
<td>1.0</td>
<td>1.0</td>
</tr>
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</table>

Sites>> CMA & NHA nine All US All US

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* As reported in Miller et al. (2012)
** PRELIMINARY for 2010; Scaled to total US Cᵣ emission of 1.6 PgC yr⁻¹