Improving Estimates of High Global Warming Potential Gas Emissions for California

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Outline

- Overview of Halocarbons
- The Global Context
- California HGWP Gas Emissions
- Methods
- Results
- Discussion/Conclusion
Overview of Halocarbons

- Halocarbons are one very predominant type of HGWP GHG; have long residence times and thus are effective GHGs despite low atmospheric concentrations (ppt).

- Include:
  - CFCs (chlorofluorocarbons)
  - HCFCs (hydrochlorofluorocarbons)
  - HFCs (hydrofluorocarbons)
  - other species (e.g. halon, CCl₄, CH₃CCl₃)

IPCC/TEAP 2005
Overview of Halocarbons

- **Source:** anthropogenically released into the atmosphere

- **Sinks:**
  - oxidation by OH in the troposphere (dominant sink)
  - wet deposition (via rain, snow)
  - dissolution
  - photolysis (photodissociation)
Tropospheric oxidation by OH

(main halocarbon sink)

- Photodissociation of O$_3$ and other trace gases provides sources of OH radicals in the atmosphere.

- OH then reacts with trace gases (e.g. halocarbons), often as the first and rate-determining step of a reaction chain that leads to oxidation of the gas.

\[
\begin{align*}
O_3 + h\nu &\rightarrow O(^1D) + O_2 \\
O(^1D) + H_2O &\rightarrow OH + OH
\end{align*}
\]
Overview of Halocarbons

- Usually Cl or Br atom reacts with O atom from O₃, thus depleting O₃ (Br significantly more reactive)
- Halocarbon-induced destruction of the stratospheric O₃ allows outgoing IR radiation to escape out of the atmosphere, causing a local radiative cooling effect in the stratosphere

IPCC/TEAP 2005
Ultraviolet radiation strikes a CFC molecule...

...and causes a chlorine atom to break away.

The chlorine atom collides with an ozone molecule...

...and steals an oxygen atom to form chlorine monoxide and leave a molecule of ordinary oxygen.

When a free atom of oxygen collides with the chlorine monoxide...

...the two oxygen atoms form a molecule of oxygen. The chlorine atom is thus released and free to destroy more ozone.
Overview of Halocarbons

- However, halocarbons themselves absorb outgoing IR (local radiative warming effect).
- Ultimately halocarbons result in a positive net radiative forcing.
- In addition, most are dangerous due to their ability to deplete O$_3$ and to allow more incoming UV radiation to reach earth’s surface.
Overview of Halocarbons

- CFCs lack an H atom thus lead to **chlorine-catalyzed O$_3$ depletion** in the stratosphere
- HCFCs contain an H atom and thus are **oxidized more readily by OH radicals** in the troposphere
  - Thus HCFCs have shorter atmospheric lifetimes and a **lower potential for depleting O$_3$**
- HFCs do not contain a Cl atom and thus do not deplete O$_3$
  - Will begin replacing HCFCs over time … but are **still effective GHGs**

(Atkinson et. al.; Fenhann 2000)
Current (Data between 2004-2008) Global Tropospheric Mixing Ratios

**CFC-11:** ~ 250 ppt
**CFC-12:** ~ 530 ppt
**CFC-113:** ~ 80 ppt

**HCFC-141b:**
- NH: ~ 20 ppt
- SH: ~ 17 ppt

**HCFC-142b:**
- NH: ~ 18 ppt
- SH: ~ 16 ppt

**CCl₄:**
- NH: ~ 95 ppt
- SH: ~ 90 ppt

**SF₆:** ~ 5-8 ppt

IPCC/TEAP (2005); WMO 2008
Mass Emission Rates (kt/yr) from 1990-2002

IPCC/TEAP 2005
Total Radiative Forcing, Pre-Industrial to Present

- Total radiative forcing for all halocarbons (present-day): **0.34 Wm$^{-2}$ ± 0.03 Wm$^{-2}$** (Houghton, *Global Warming* )

- Total radiative forcing for CO$_2$: **1.46 Wm$^{-2}$** (Houghton, *Global Warming* )

- Total radiative forcing for all GHG: **2.43 Wm$^{-2}$**

- Ratio of total radiative forcing for all halocarbons to total radiative forcing for CO$_2$: ~ **23.29%**
  - i.e. the amount of radiative forcing induced by halocarbons is ~ 23.29% of that induced by CO$_2$

- Ratio of total radiative forcing for all halocarbons to total radiative forcing for all GHG: ~ **13.99%**
  - i.e. the amount of radiative forcing induced by halocarbons is ~ 13.99% of that induced by all GHG
Main sources of HGWP gases in CA according to the California Energy Commission:

- Substitutes for ODSs (mostly **HFCs** used as refrigerants, fire extinguishants, etc.)
- Semiconductor manufacturing (mostly *trifluoromethane, perfluoromethane, SF₆*)
- Electric utilities (mostly **SF₆**)

(CEC-600-2006 013-SF)
California HGWP Gas Emissions

- In 2004, 2.9% of the total 492 MtCO$_2$Eq of emissions in CA were from HGWP gases
  - **Increasing at a faster rate** than any other group of GHGs
  - Small amounts of HGWP gases are emitted, but are dangerous because of their **high potential**
  - With a potential 22,200 times greater than CO$_2$, SF$_6$ has the highest known GWP of all GHG gases
CEC MtCO₂EQ Values for HGWP Gases

- Total 2004 HGWP Gas Emissions: 14.20 MtCO₂Eq
  - Substitutes for ODSs: 12.61 MtCO₂Eq
  - Semiconductor man. : 0.57 MtCO₂Eq
  - Electric utilities: 1.02 MtCO₂Eq

- Total HGWP gas emissions projected to increase to 33-38 MtCO₂Eq by 2020
Relevance to California Policy

- California Global Warming Solutions Act of 2006 requires the state to reduce total GHG emissions to:
  - **1990 levels by 2020** (30% of total current emissions)
  - **80% below 1990 levels by 2050**

- Assuming the projected increase is accurate, HGWPs will account for **7.7 to 8.9%** of the 1990 emission levels in 2020
ARB Emissions Inventory

1990 Emission Baseline

~169 MMT CO₂e Reduction

80% Reduction ~341 MMT CO₂e
Methods

- Atmospheric Measurements
  - Walnut Grove Tower
- Radon Tracer Method
Methods: Atmospheric Measurements

- Measurements taken at **Walnut Grove Tower** (in Sacramento County, left)

- For our study, data from October 2007 – December 2007 was used
Methods: Atmospheric Measurements

- Rn measurements also taken on site at LBL
Methods: Radon Tracer Method

- **Uranium** is ubiquitous in rocks, found in varying concentrations (high in granitic rock)
- Radon is a daughter product formed by the radioactive decay of uranium

(U.S. Geological Survey)
Methods: Radon Tracer Method

Factors that control radon movement:
- Soil moisture content
- Soil porosity
- Soil permeability

U.S. Geological Survey
Methods: Radon Tracer Method

- Use **radon** as an atmospheric tracer gas
  - **Tracer**: a small amount of radioactive isotope introduced into a system in order to follow the behavior of some component of that system
  (lbl.gov)
Methods: Radon Tracer Method

- Why might we think $^{222}\text{Rn}$ is a useful atmospheric tracer gas for time-series data? (i.e. why might we think $^{222}\text{Rn}$ and the HGWP gases covary significantly?)
  - $^{222}\text{Rn}$ and many GHGs are exchanged between the biosphere and the atmosphere near the Earth’s surface and thus both undergo the same atmospheric mixing processes
  - $^{222}\text{Rn}$ has a half-life of 3.8 days and the process by which it is lost in the atmosphere is well understood
Methods: Radon Tracer Method

- Estimate fluxes of HGWP gases

\[ F_{GHG} = F_{Rn} \times \left( \frac{\Delta [GHG]}{\Delta [Rn]} \right) \]

- \( F_{GHG} \) = average footprint-weighted biosphere atmosphere flux of GHG

- \( F_{Rn} \) = average footprint-weighted soil atmosphere flux of \(^{222}\)Rn

- \( \Delta [\text{gas}] \) = difference between concentration of gas present in atmosphere and ambient concentration of gas

- \( \left( \frac{\Delta [GHG]}{\Delta [Rn]} \right) = \text{linear slope of a best-fit line} \) obtained by performing a linear regression with time series data of \([GHG]/[Rn]\)
Calculating CO$_2$ Equivalent Emission Rate via Radon Tracer Method

- **Estimate** $F_{Rn}$
  - Aforementioned equation can be used only if we have reasonable regional estimates for $F_{Rn}$!
  - $^{222}\text{Rn}$ concentration measured at Walnut Grove Tower from October 2007 – December 2007
  - Convert the concentration to a footprint average $^{222}\text{Rn}$ flux for the region
  - Use this footprint average flux value for $F_{Rn}$ in the aforementioned equation to measure fluxes for each of the HGWP gases that we collected data for
Calculating CO₂ Equivalent Emission Rate

- Convert each HGWP Gas flux to an emission rate, and then to an equivalent CO₂ emission rate.
  - Air has a molar density of 42.02 mol/m³, assuming that gases behave ideally.
  - Assume standard atmospheric pressure of 1 atm, and a temperature of 290K.
  - Assume footprint-average ²²²Rn flux value is spatially constant (fairly good assumption).
  - Assume area of the ²²²Rn emissions = Area of emission of each HGWP gas (more on this later).
Calculating CO₂ Equivalent Emission Rate

- CO₂ Equivalent Emission Rate Formula:

\[
E_{\text{CO}_2,\text{eq},X} \text{ (Million Metric Tons CO}_2\text{EQ)} = E_X \cdot m_X \cdot (10^{-12}\text{mol/pmol}) \cdot GWP_X
\]
\[
(\text{g CO}_2/\text{g X}) \cdot (1\text{megaton}/10^{12}\text{g}) \cdot (3.15 \times 10^7\text{ sec/yr})
\]

- \(E_{\text{CO}_2,\text{eq},X}\) = equivalent CO₂ emission rate of gas X
- \(E_X\) = emission rate of gas X (pmol/s)
- \(m_X\) = molecular weight of gas X (g/mol)
- \(GWP_X\) = global warming potential of gas X
- 1 megaton = 1 million metric tons = 10^{12} grams
Results

- Regression Plots
Results: Regression Plots

- Regression plots for some of the HGWP gases
- Slope values for these plots were used in our calculations for HGWP fluxes and eventually equivalent CO$_2$ emissions
- Uncertainties in slopes range from $\sim7$-$\sim15\%$
Discussion

- Estimate for Total CO$_2$ Equivalent Emissions
- Comparison with existing inventories
- Halocarbons with high emissions
- Sources of error
Discussion: Estimation and Comparison with Existing Inventories

- Our estimate for total HGWP gas emission (not including CFCs) = \(12.0 \text{ MtCO}_2\text{Eq}\)
- Emissions estimates for each gas have uncertainties ranging from 8 to 17%
- CEC 2004 estimate = \(14.2 \text{ MtCO}_2\text{Eq}\)
- We used 14 total gases in our estimate, including important ones like SF\(_6\) and HFC-134a
Discussion: Comparison With Existing Inventories

- Our area of emissions was **149,921 km\(^2\)**, the total area of counties with population \(> 500,000\).
  - All of the major **industrial** areas included in the estimate (LA County, SF County, Sacramento County, etc.)
- Although this is only **37.1%** of the total area of California, the number of residents account for **82.6%** of the total population of the state.
Discussion: Comparison With Existing Inventories

- If we include all counties with populations >200,000, we increase our area estimate by about 50,000 km$^2$
  - This increase in area increases the estimate of total emissions by ONLY ~4MtCO$_2$Eq!
  - Including these counties would account for 94% of the total population of California!

- Conclusion: area not a big source of error, and our estimate is reasonable
Discussion: Comparison With Existing Inventories

- Our estimate for total CFC gas emission = \(10.9 \text{ MtCO}_2\text{Eq}\) (almost equal to our total HGWP gas emission)
- CFCs are not included in the CEC inventory because they are assumed to have 0 emissions since they have been banned
- However, considering our CFC emission estimate is almost equal to our total HGWP gas emission estimate, these gases are significant
Discussion: Halocarbons with high emissions

- HCFC-22 (6.9 MtCO$_2$Eq/yr)
- HFC-134a (3.3 MtCO$_2$Eq/yr)
- CFC-12 (6.4 MtCO$_2$Eq/yr)
- CFC-11 (3.7 MtCO$_2$Eq/yr)
HCFC-22

- **6.9 MtCO$_2$Eq;** global conc. *increasing*; global emission rate *steady*
- Refrigerant
  - residential uses: window AC units, dehumidifiers, central AC, and ground source heat pumps
  - commercial uses: packaged AC units, chillers, cold storage warehouses, and retail food refrigeration
- **Many substitutes available** - both Class I and Class II substitutes for ODSs
HFC-134a

- **3.3 MtCO₂ Eq;** global conc. increasing; global emission rate increasing
- Refrigerant used for residential refrigeration and automobile AC; also used as foam blower
- Implemented as a substitute for CFC-12
- In 2008, California's Air and Resource Board held 2 public workshops that focused on actions to phase out HFC-134a due to its high GWP
- ~ **2.5 MtCO₂ Eq reduction** by 2020 if there is a complete phaseout of HFC-134a
CFC-12

- 6.4 MtCO$_2$Eq; global conc. steady; global emission rate decreasing
- Refrigerant used mainly in automobile AC systems
- Production was banned in 1994 but is still being recycled and reused
- One of the most dangerous halocarbons:
  - ODP of 1
  - GWP of 10,900
CFC-11

- **3.7 MtCO₂ Eq;** global conc. **decreasing**; global emission rate **decreasing**
- Ideal refrigerant because its high boiling point places less stress on an operating system
- Banned in 1995
Discussion: Sources of Error

- Estimation of footprint-weighted $^{222}\text{Rn}$ flux
- Covariance between $^{222}\text{Rn}$ and each HGWP gas
- Assumption that the area of $^{222}\text{Rn}$ flux is equal to the area of each HGWP gas flux
- Assumption that the background $F_{\text{Rn}}$ flux is uniform across the area over which measurements were taken
- Total area of emissions (already addressed)
Summary

- Globally, HFCs are increasing and replacing CFCs, HCFCS
  - According to our data, CFCs and HCFCs are still being emitted at significant rates across California
- Radon transport method is reliable and useful for most HGWP gases, unreliable for others
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References


References


