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, CCl_4, CH_3CCl_3)

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**

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

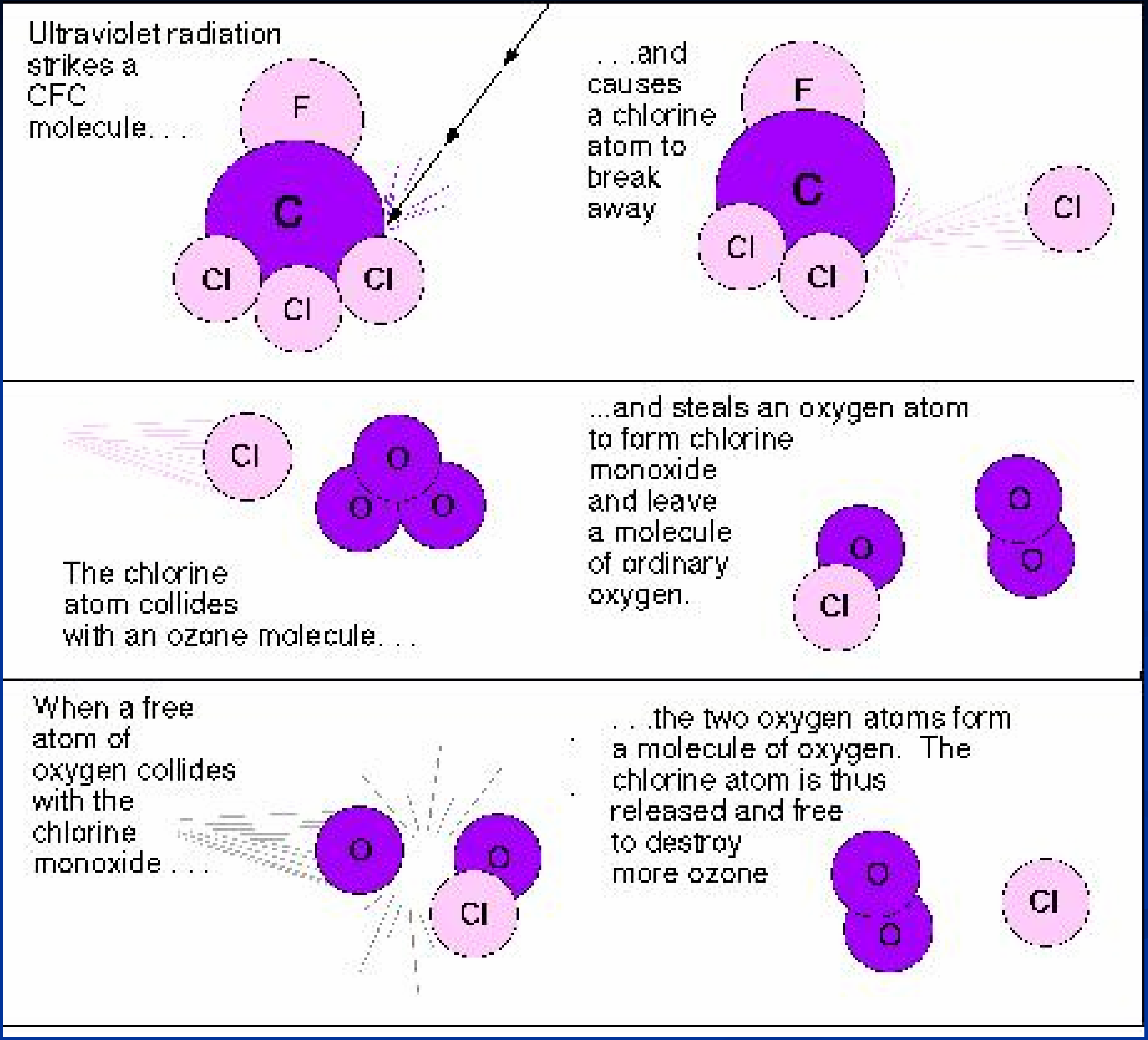
$$O(^1D) + H_2O \rightarrow OH + OH$$

IPCC/TEAP 2005

Overview of Halocarbons

- Usually *Cl* or *Br* atom reacts with O atom from O_3, thus depleting O_3 (Br significantly more reactive)
- Halocarbon-induced destruction of the stratospheric O_3 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. . .
F
C
Cl
Cl
Cl
. . .and causes a chlorine atom to break away
F
C
Cl
Cl
Cl
Cl
O
O
O
The chlorine atom collides with an ozone molecule. . .
...and steals an oxygen atom to form chlorine monoxide and leave a molecule of ordinary oxygen.
O
Cl
O
O
When a free atom of oxygen collides with the chlorine monoxide . . .
O
O
Cl
. . .the two oxygen atoms form a molecule of oxygen. The chlorine atom is thus released and free to destroy more ozone
O
O
Cl

albany.edu

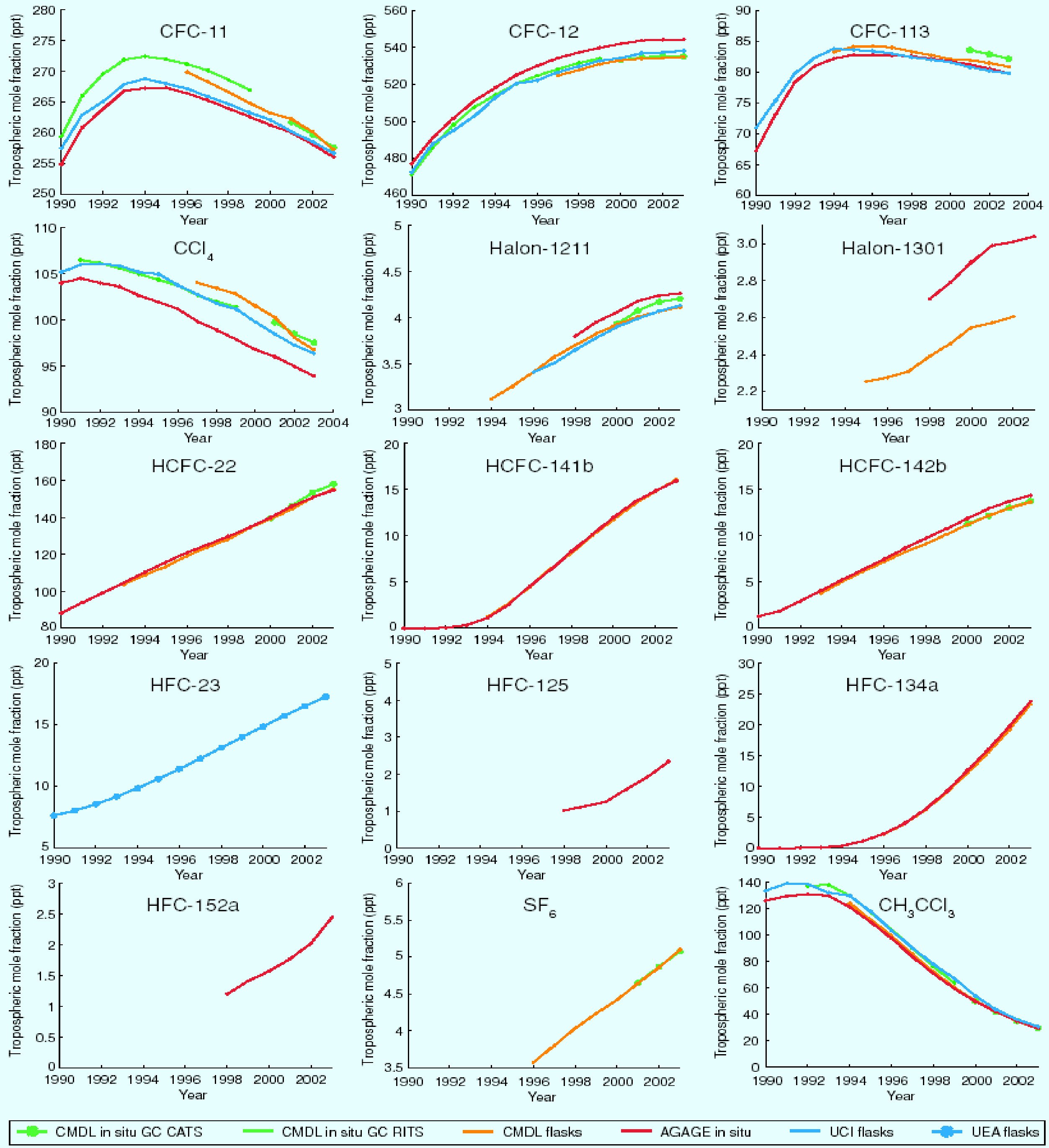
Overview of Halocarbons

- 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)



IPCC/TEAP (2005); WMO 2008

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**

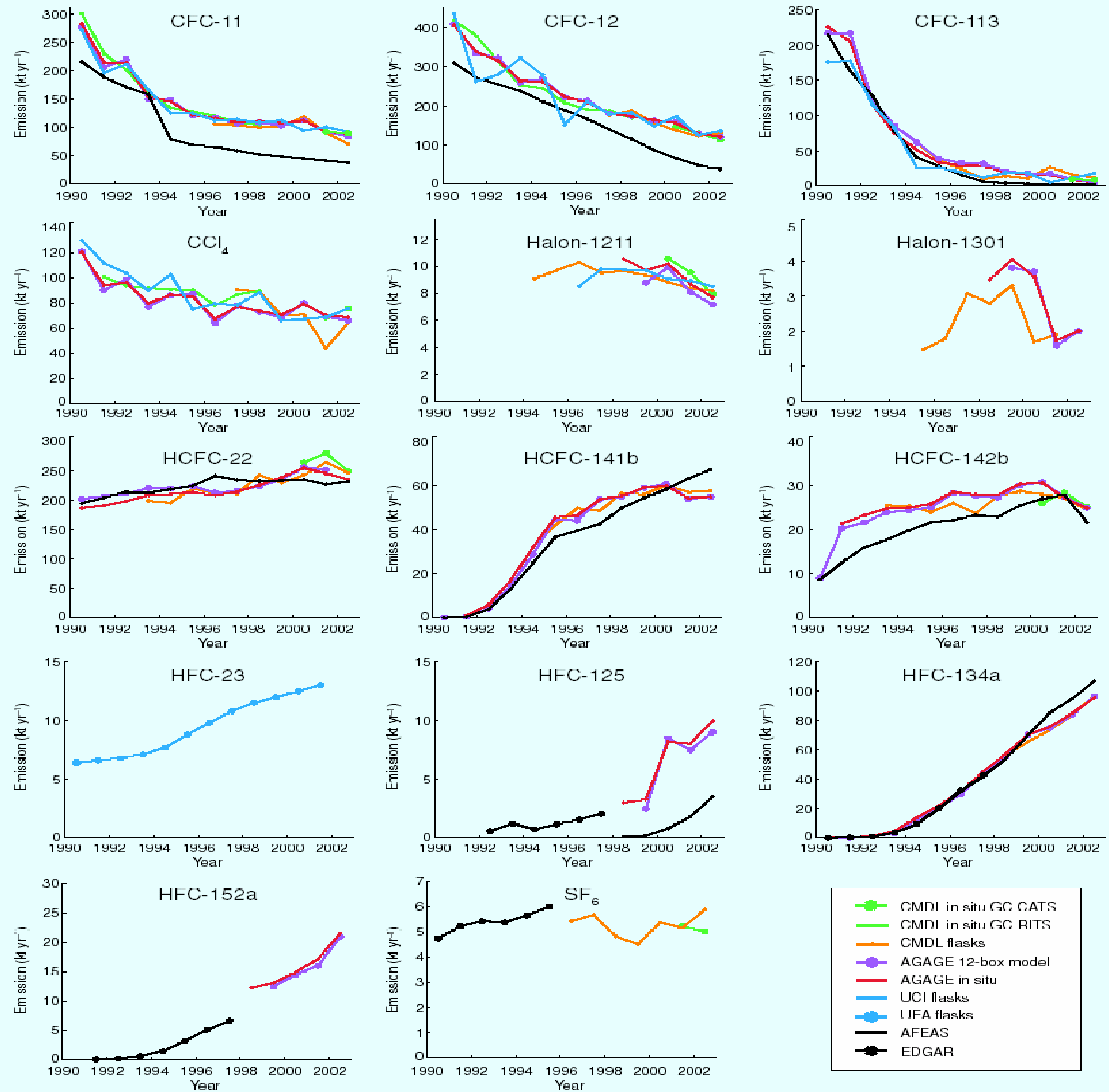
SH: ~ **16 ppt**

CCl_4:

NH: ~ **95 ppt**

SH: ~ **90 ppt**

SF_6: ~ **5-8 ppt**



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): **$0.34\ Wm^{-2} \pm 0.03\ Wm^{-2}$** (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

California HGWP Gas Emissions

- 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, SF_6**)
  - Electric utilities (mostly **SF_6**)

(CEC-600-2006 013-SF)

California HGWP Gas Emissions

- In 2004, **2.9%** of the total 492 $MtCO_2Eq$ 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 $MtCO_2EQ$ Values for HGWP Gases

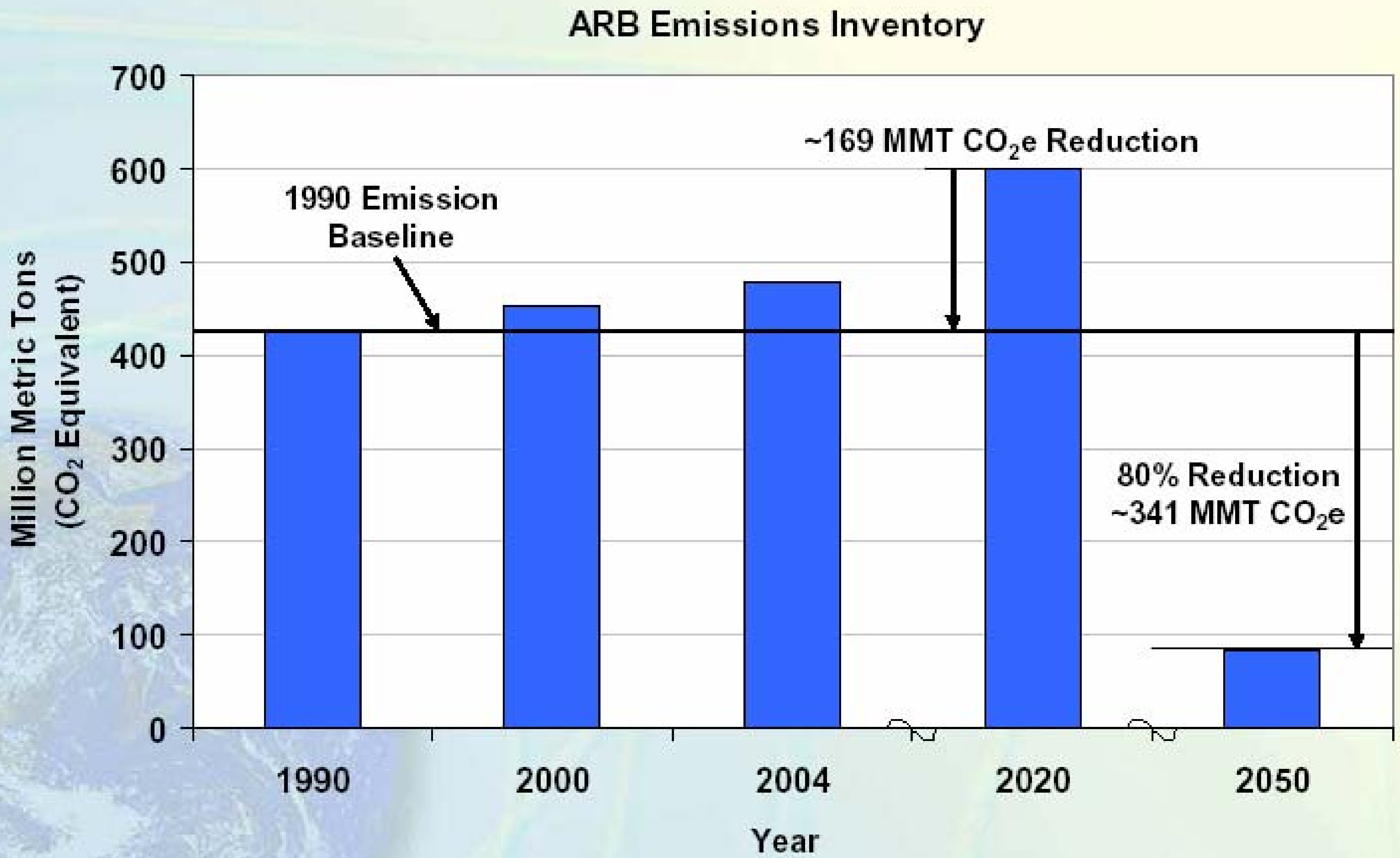
- Total 2004 HGWP Gas Emissions:

  14.20 $MtCO_2Eq$
  - Substitutes for ODSs: **12.61 $MtCO_2Eq$**
  - Semiconductor man. : **0.57 $MtCO_2Eq$**
  - Electric utilities: **1.02 $MtCO_2Eq$**
- Total HGWP gas emissions projected to increase to **33-38 $MtCO_2Eq$ by 2020**

CEC 2006

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
Million Metric Tons (CO_2 Equivalent)
700
600
500
400
300
200
100
0
1990 Emission Baseline
~169 MMT CO_2e Reduction
80% Reduction
~341 MMT CO_2e
1990
2000
2004
2020
2050
Year

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

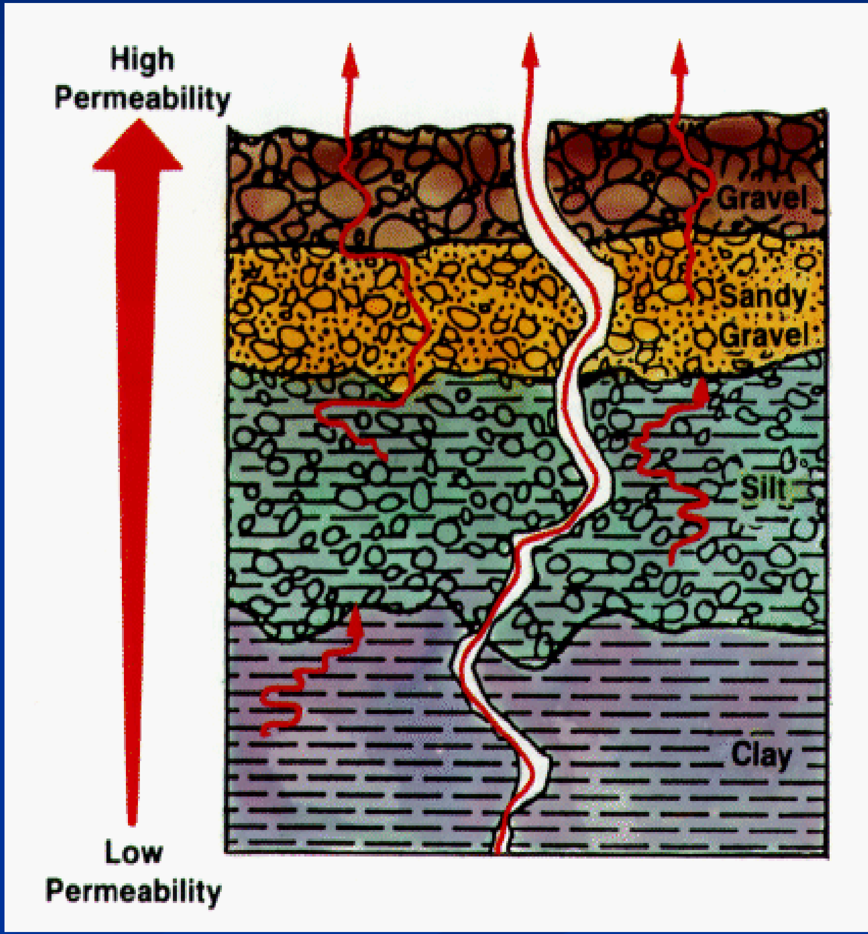
Methods: Radon Tracer Method

- **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}Rn is a useful atmospheric tracer gas for time-series data? (i.e. why might we think ^{222}Rn and the HGWP gases **covary** significantly?)
  - ^{222}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}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
- $F_{GHG} = F_{Rn} * [(\Delta[GHG])/(\Delta[Rn])]$
  - F_{GHG} = average **footprint-weighted** biosphere → atmosphere flux of GHG
  - F_{Rn} = average **footprint-weighted** soil → atmosphere flux of ^{222}Rn
  - Δ [] = difference between concentration of gas present in atmosphere and ambient concentration of gas
- $(\Delta[GHG])/(\Delta[Rn])$ = **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}Rn **concentration** measured at Walnut Grove Tower from October 2007 – December 2007
  - Convert the concentration to a **footprint average ^{222}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 CO_2 Equivalent Emission Rate

- Convert each **HGWP Gas flux** to an **emission rate**, and then to an **equivalent CO_2 emission rate**
  - Air has a **molar density** of 42.02 mol/m^3, assuming that gases behave **ideally**
  - Assume standard atmospheric pressure of **1 atm**, and a temperature of **290K**
  - Assume footprint-average ^{222}Rn flux value is **spatially constant** (fairly good assumption)
  - Assume area of the ^{222}Rn emissions = Area of emission of each HGWP gas (more on this later)

Calculating CO_2 Equivalent Emission Rate

- CO_2 Equivalent Emission Rate Formula:

$E_{CO2,eq,X}$ (Million Metric Tons CO_2EQ) = E_X * m_X * (10^{-12}mol/pmol) * GWP_X (g CO_2/g X) * (1megaton/10^{12}g) * (3.15 x 10^7 sec/yr)

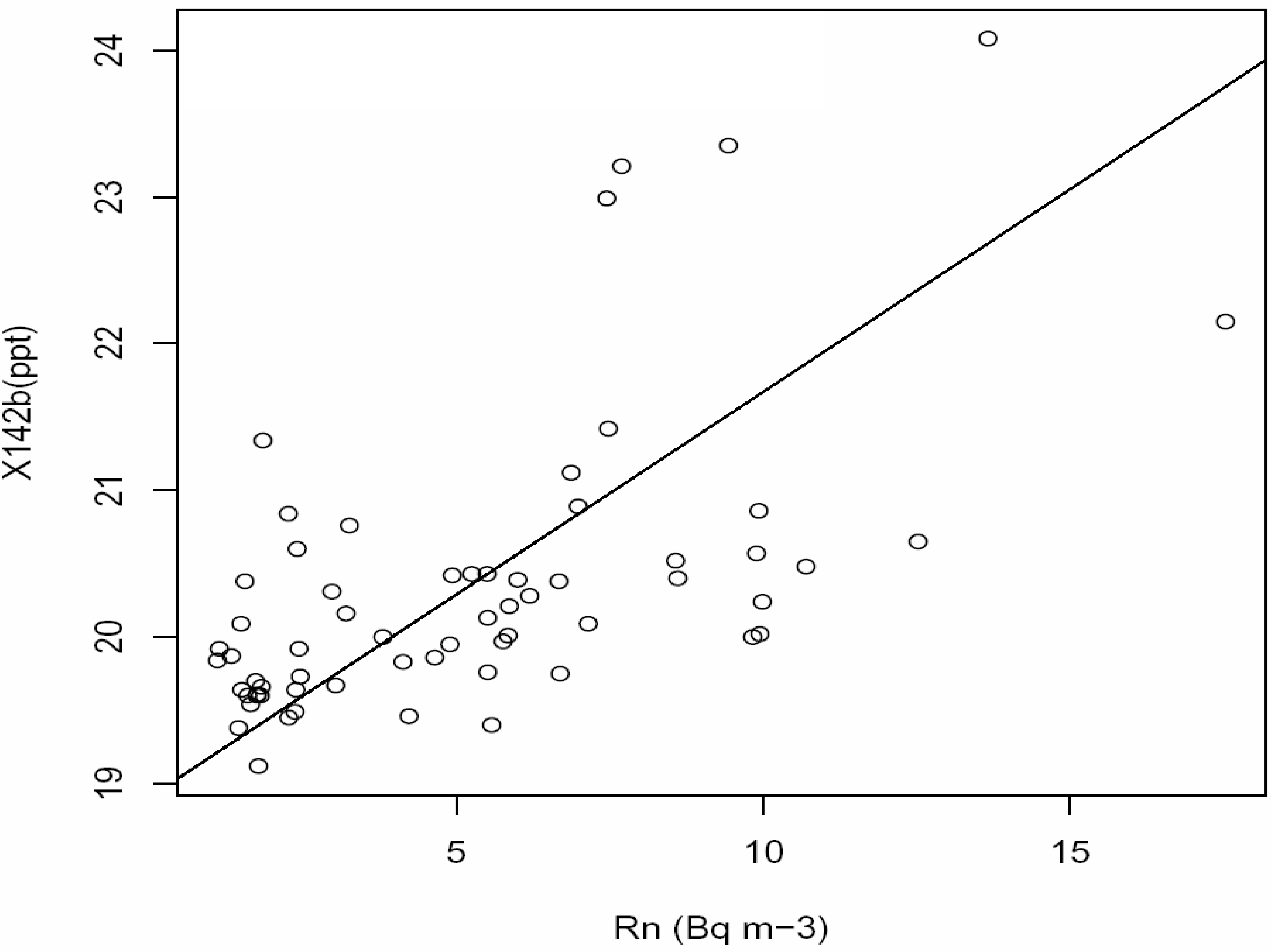
- **$E_{CO2,eq,X}$** = equivalent CO_2 emission rate of gas X
- **E_X** = emission rate of gas X (pmol/s)
- **m_X** = molecular weight of gas X (g/mol)
- **GWP_X** = global warming potential of gas X
- 1 megaton = 1 million metric tons = 10^{12} grams

Results

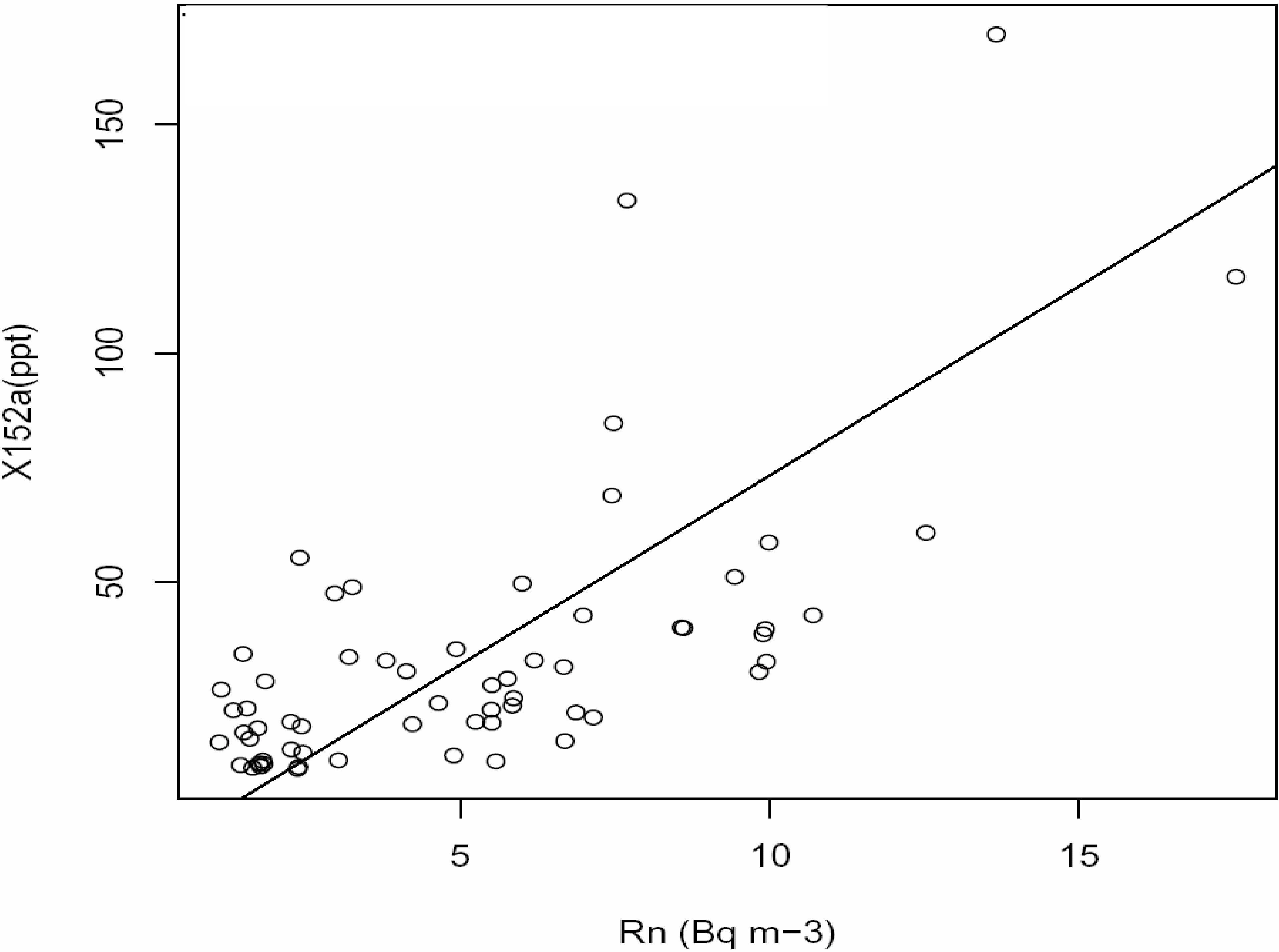
- Regression Plots

Results: Regression Plots

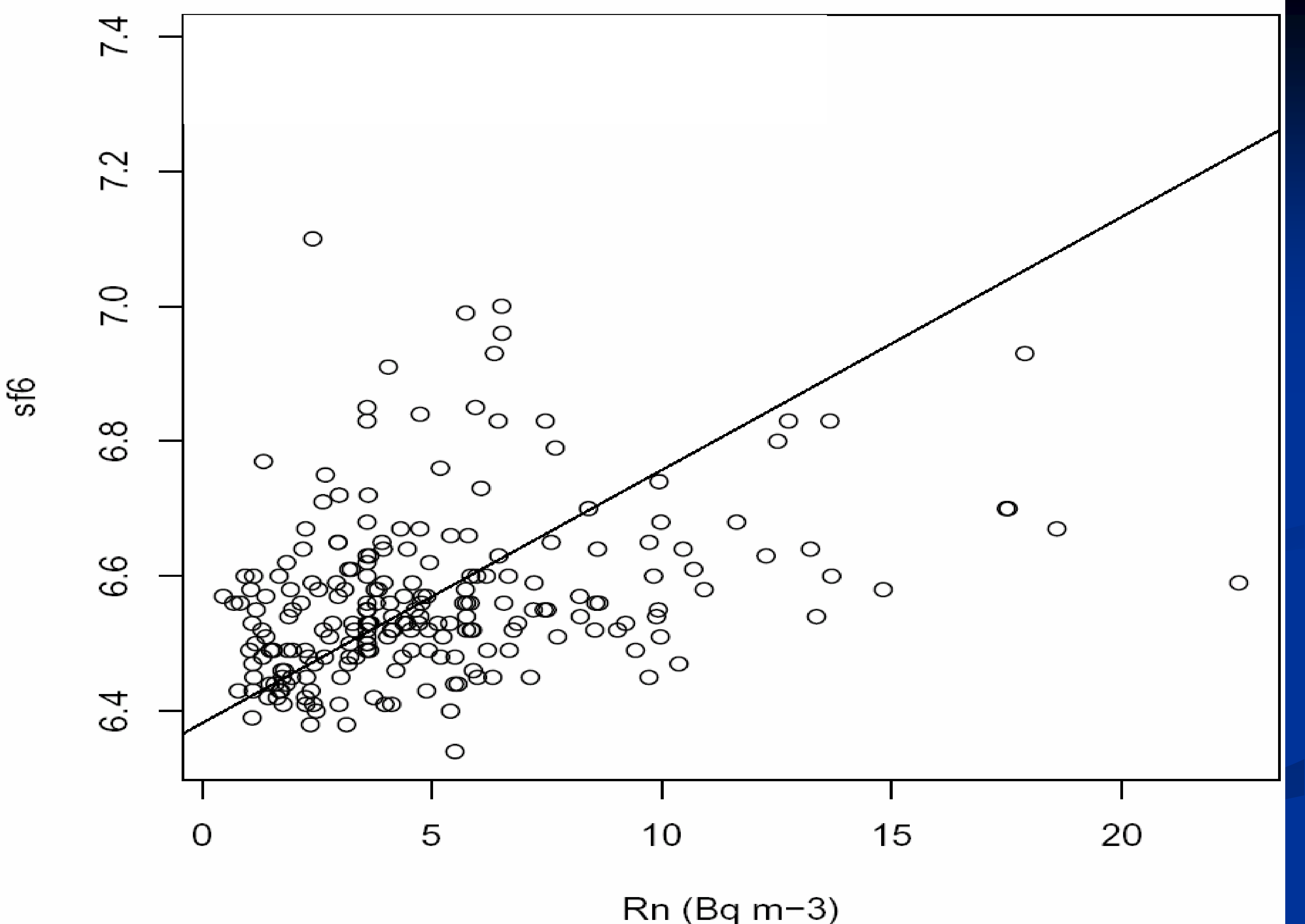
- Regression plots for some of the HGWP gases
- Slope values for these plots were used in our calculations for HGWP fluxes and eventually equivalent CO_2 emissions
- Uncertainties in slopes range from **~7-~15%**



X142b(ppt)
19
20
21
22
23
24
5
10
15
Rn (Bq m−3)



150
100
50
X152a(ppt)
5
10
15
Rn (Bq m-3)



sf6
7.4
7.2
7.0
6.8
6.6
6.4
0
5
10
15
20
Rn (Bq m−3)

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 $MtCO_2Eq$**
  - **Emissions estimates for each gas have uncertainties ranging from 8 to 17%**
- CEC 2004 estimate =**14.2 $MtCO_2Eq$**
- 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 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_2Eq!**
  - **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 $MtCO_2Eq$** (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 $MtCO_2Eq$**; 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 $MtCO_2Eq$**; 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 $MtCO_2Eq$ reduction** by 2020 if there is a complete phaseout of HFC-134a

CFC-12

- **6.4 $MtCO_2Eq$**; 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 $MtCO_2Eq$**; 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}Rn flux
- Covariance between ^{222}Rn and each HGWP gas
- Assumption that the area of ^{222}Rn flux is equal to the area of each HGWP gas flux
- Assumption that the background F_{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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