The special treatment for the Fitzgerald trucks is made possible by a loophole in federal law that the Obama administration tried to close, and the Trump administration is now championing. The trucks, originally intended as a way to reuse a relatively new engine and other parts after an accident, became attractive for their ability to evade modern emissions standards and other regulations. That makes them cheaper to operate, but means that they spew 40 to 55 times the air pollution of other new trucks, according to federal estimates.
Human activities have altered the chemical composition of the atmosphere through the buildup of greenhouse gases – primarily carbon dioxide, methane, and nitrous oxide.

The heat-trapping property of these gases is undisputed although uncertainties exist about exactly how earth’s climate responds to them.

Estimated increase of 2.2-10°F (1.4-5.8°C) in the next century!! Evaporation will increase as the climate warms, which will increase average global precipitation. Soil moisture is likely to decline in many regions, and intense rainstorms are likely to become more frequent. Sea level is likely to rise two feet along most of the U.S. coast.

http://yosemite.epa.gov/oar/globalwarming.nsf
Absorption of terrestrial radiation by H₂O and CO₂ and atmospheric window: 8000-12000nm

TABLE 4-1  Summary of Information About Some Greenhouse Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Current concentration</th>
<th>Residence time, in years</th>
<th>Relative global warming efficiency, 100-year horizon</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>373 ppm</td>
<td>50–200</td>
<td>1</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.77 ppm</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>N₂O</td>
<td>316 ppb</td>
<td>120</td>
<td>296</td>
</tr>
<tr>
<td>CFC-11</td>
<td>0.26 ppb</td>
<td>45</td>
<td>4600</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>0.15 ppb</td>
<td>12</td>
<td>1700</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>0.01 ppb</td>
<td>14</td>
<td>1300</td>
</tr>
<tr>
<td>Halon-1301</td>
<td>0.003 ppb</td>
<td>65</td>
<td>6900</td>
</tr>
</tbody>
</table>

From Spiro book
Atmospheric Residence Time

\[
\frac{dC}{dt} = -kC \\
\int \frac{dC}{C} = -kt + \text{constant} \\
\ln C = -kt + \text{constant}
\]

At \( t=0 \), \( \ln C_0 = \) constant
\( \ln C = \ln C_0 - kt \)
\[\therefore \ln \left( \frac{C}{C_0} \right) = -kt \quad \text{Or} \quad C/C_0 = e^{-kt}\]

Rate of decline in terms of half life
Or time corresponding to \( C=0.5C_0 \)
\[\ln(0.5C_0/C_0) = -kt_{1/2}\]
\[0.693 = kt_{1/2} \quad \text{or} \quad t_{1/2} = 0.693/k\]

At steady state, \( R = kC \) or \( C_{ss} = R/k \)
\[C_{ss} = \frac{Rt_{1/2}}{0.693} \quad \text{or} \quad C_{ss} = 1.44t_{1/2}\]

Average Residence Time

Every atmospheric gas existing at or near steady state has a characteristic residence time \( t_{avg} \)

\( t_{avg} \) - Time required for its overall concentration to fall \( 1/e \) times the initial value (\( e \) is the base of natural logarithms).

At \( t = t_{avg} \), \( C = C_0/e \)
\[\ln(C_0/e)/C_0 = -kt_{avg}\]
\[\ln(1/e) = -1 \quad \therefore t_{avg} = 1/k\]

Since \( C_{ss} = R/k \) we can write
\[C_{ss} = R \times t_{avg} \quad \text{or} \quad t_{avg} = C_{ss}/R\]

Example: If steady state concentration of a gas is 10 ppm and input rate is 2 ppm/year, then we can determine the average residence time,
\[t_{avg} = C_{ss}/R \quad t_{avg} = 10 \text{ ppm}/(2 \text{ ppm/year}) = 5 \text{ years}\]
Methane

- \((3n-6)=9\) vibrational modes
- Because of the symmetry many of the vibrational modes are inactive
- H-C-H stretching vibrations occur well outside the thermal region
- HCH bond-angle-bending vibrations absorb at 7.7 \(\mu m\)
- Per molecule absorb greater fraction of IR than \(CO_2\) - 23 times

Methane

Methane (\(CH_4\)) is the most abundant organic trace gas in the atmosphere (mixing ratio, 1.8 ppm) and is important to both tropospheric and stratospheric chemistry.

Its atmospheric concentration has almost tripled since pre-industrial times.

It plays a central role in atmospheric oxidation chemistry and affects stratospheric ozone and water vapor levels.

Most of the methane from natural sources in Earth's atmosphere is thought to originate from biological processes in anoxic environments.
Greenhouse gas emissions from livestock, such as the pigs shown in this Photodisc image, can be reduced with biofiltration of methane.

Most hogs in the U.S. are raised in confinement buildings where all manure is in liquid form and is stored in lagoons or in pits under the confined building. This liquid manure emits many gases, including methane, carbon dioxide, ammonia, and hydrogen sulfide, mainly due to anaerobic decomposition.

Emission sources:
- Natural wetlands, fossil fuels, landfills, animals, rice paddy and biomass burning
- 70% of current methane emissions are anthropogenic in origin
- Anaerobic decomposition: \((-\text{CH}_2\text{O}-)_n \rightarrow \text{CH}_4 + \text{CO}_2\)

Leveled off during last 20 years
Methane Hydrate $\text{CH}_4\cdot6\text{H}_2\text{O}$

• Found at the bottom of the ocean
• Methane is caged in a 3-D ice lattice structure
• Relatively higher melting point ($18^\circ\text{C}$) compared to ice
• Warmer sea may initiate the release of methane

Hydrate deposits may be several hundred meters thick and generally occur in two types of settings: under Arctic permafrost, and beneath the ocean floor.

Sink for Methane

Unlike CO₂ methane has an average lifetime of about a decade

\[ \text{CH}_4 + \cdot \text{OH} \rightarrow \cdot \text{CH}_3 + \text{H}_2\text{O} \]

This reaction is followed by its oxidation to CO₂

\[ \text{CH}_4 \rightarrow \text{CH}_2\text{O} \rightarrow \text{CO} \rightarrow \text{CO}_2 \]

~90% of 530 Tg/year methane is converted by this route

Any methane that escapes in stratosphere reacts with excited oxygen atom

\[ \text{CH}_4 + \text{O}^* \rightarrow \cdot \text{OH} + \text{CH}_3 \]

\[ \text{CH}_4 + \cdot \text{OH} \rightarrow \cdot \text{CH}_3 + \text{H}_2\text{O} \]

…..also responsible for increase in the water vapor in stratosphere

Emission Trends:

The methane concentration has doubled (from 0.75 ppm to 1.77 ppm in 2002)

Stabilized emission from rice paddies and decreased emissions from pipelines are possible reasons for recent stabilization in CH₄ emission
After 2000-era plateau, global methane levels hitting new highs

- The trouble is methane’s lifetime isn’t constant.
- Hydroxyl radical isn’t something we can measure directly at a global scale
- The abundance of hydroxyl radical varies enough over time and plays a role in the stop and go trajectory of methane levels in recent decades.
- The post-2007 uptick in global methane levels roughly coincides with the rapid deployment of natural gas “fracking” in the United States, making fugitive emissions a logical suspect.

Currently, methane emissions exceed removal rates by about 10 million tons per year.

(NOAA Climate.gov graphic)

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**Nitrous Oxide**

\[ \text{N}_2\text{O} \]

Bond bending vibrations absorb at 8.6 µm
Bond stretching vibrations is centered at 7.8 µm

*Per molecule basis, N\textsubscript{2}O is 296 times more effective as CO\textsubscript{2} in global warming*

Relatively low concentration in atmosphere -316 ppb in 1990
Less than 40% of N\textsubscript{2}O is anthropogenic

Most of the anthropogenic N\textsubscript{2}O comes from the increased use of Fertilizers
Landfills may also contribute as a result of denitrification processes.

There is no sink for N\textsubscript{2}O in the troposphere. It rises to stratosphere and
gets decomposed by the absorption of UV-light to produce N\textsubscript{2} and O or
reacts with oxygen atom.

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**Denitrification**

![Denitrification Diagram](image)
CFCs and Their Replacements

The atmospheric window for IR is 8-12 $\mu$m region. Many of C-Cl bond stretch and bond angle bending vibrations occur in this region. C-F bond stretch occurs at 9 $\mu$m.

Due to high efficiency of IR absorption and long life in the atmosphere, CFCs and CF$_2$Cl$_2$ molecules can be significant contributors to global warming.

However, the net effect is regarded as small. The heating is offset by cooling effect caused during the destruction of ozone.

CFC replacements (HFC and HCFCs have shorter lifetime but greater emission in the coming decades can become a point of concern.

Ozone in the troposphere

- Greenhouse gas that has mostly of anthropogenic origin
- Relatively short lifetime
- Bending vibrations at 14 $\mu$m and stretching vibrations between 9-10 $\mu$m
- Can contribute up to 10% of increased global warming
Climate Modifying Effects of Aerosols

A fraction of light entering the earth atmosphere fails to reach earth surface because of back scattering (Albedo)

Light absorption by aerosol and dissipation as heat (e.g., dark soot particles)

Sulfate aerosol

Origin: SO₂ released from burning of fossil fuels, especially coal

- Do not absorb sunlight, hence do not contribute directly to global warming
- These aerosols reflect the incident light and hence less amount of sunlight reach the earth surface
- The net effect is to cool the air near the ground surface. Thus offsets some of the effects of GHG
- One recent example is the effect of Mt. Pinatubo volcano in 1991. 30 million tonnes of SO₂ formed sulfate aerosol after its oxidation in the atmosphere.

Result: Several cool summers in Northern America in early 1990s.
Mt. Pinatubo eruption made 1992 one of the coolest year

Largest eruption since 1912

Red line: modeled temperature changes
Blue line: temperature changes observed from meteorological ground stations

http://www.ngdc.noaa.gov/seg/hazard/stratoguide/pinfact.html
http://vulcan.wr.usgs.gov/Volcanoes/Philippines/Pinatubo/description_pinatubo.html

The New York Times

October 24, 2007
OP-ED CONTRIBUTOR
How to Cool the Globe
By KEN CALDEIRA

DESPITE growing interest in clean energy technology, it looks as if we are not going to reduce emissions of carbon dioxide anytime soon. The amount in the atmosphere today exceeds the most pessimistic forecasts made just a few years ago, and it is increasing faster than anybody had foreseen.

One idea is to counteract warming by tossing small particles into the stratosphere (above where jets fly). This strategy may sound far-fetched, but it has the potential to cool the earth within months.

© New York Times
Henny Ray Abrams (Oct. 24, 2007)
Is this a sensible plan?

**Latitudes and Altitudes**

**Tropical:** Inject SO$_2$ into the lower stratosphere (16-22 km) over the Equator at a daily rate equal to 5 Mt/yr (1 Pinatubo every 4 years) or 10 Mt/yr (1 Pinatubo every 2 years) for 20 years, and then continue to run for another 20 years to see how fast the system warms afterwards.

**Arctic:** Inject SO$_2$ into the lower stratosphere (10-15 km) at 68°N at a daily rate equal to 3 Mt/yr for 20 years, and then continue to run for another 20 years to see how fast the system warms afterwards.


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**Impact of aerosol**

Because of the industrial activity the cooling effect of aerosol is seen in northern hemisphere.

The avg. diameter is around 0.45 mm and average altitude is around 0.5 km

Since sulfate aerosols are efficiently removed by rain, their lifetime is of the order of days

The amount of sunlight reflected into space by anthropogenic aerosols by the direct mechanism in units of watts per square meter of the earth surface

Note the values of Ohio valley
The values quoted in this chart (from the text book) are slightly different than those discussed in the previous class. The overall argument for observing warmer climate on earth is same. You may consider either the model discussed in the class or the one presented in the book.

Allocation of Warming to Natural and Anthropogenic Factors

Given our greenhouse gas emissions, the earth should have warmed considerably more than it has in reality.

Many scientists believe that the cooling effect of sulfate aerosols has made an indirect contribution.

Modeling the aerosols' effects is considered as one of the bigger challenges.
Global Warming Trend

Global surface air temperatures observed and simulated by global circulation models.

Climate Forecast Model (bbc)
http://news.bbc.co.uk/2/shared/spl/hi/sci_nat/04/climate_change/html/climate.stm

Cooling over China from Haze

In China, Cloud-free Days Do Not Mean Sunshine; Smog Is To Blame
January 18, 2006

China has darkened over the past half-century. Where has all the sunshine gone? Eliminating clouds from the dimming equation now leaves little doubt that human activity, in the form of a nine-fold increase in fossil fuel emissions over the same half-century period, has entrenched China in a foggy haze that absorbs and deflects the sun’s rays.
Solar Shield Could Tackle Global Warming

AFP

Efforts to tackle global warming through politics are falling so pitifully short of what is needed that ideas dismissed just a few years ago as weird science are now getting a serious hearing.

One novel idea is for a gigantic sunshade in space.

It comes from Roger Angel, a professor at the University of Arizona and one of the world's top authorities on optics.

His "solar shield" would comprise a spider's web of struts holding six tiltable mirrors that would deflect some of the Sun's rays away from Earth, reducing solar energy reaching our planet by two percent — enough to compensate, at least in part, for the warming effect caused by carbon emissions.

The web, measuring some 1,200 miles across, would be placed at a permanent vantage point called the Earth-Sun L1 Lagrange position, almost 950,000 miles from home.

Those who write off Angel as crazy should also tell NASA, whose Institute for Advanced Concepts (NIAC) last month asked him to flesh out the basic proposal into something more detailed.
