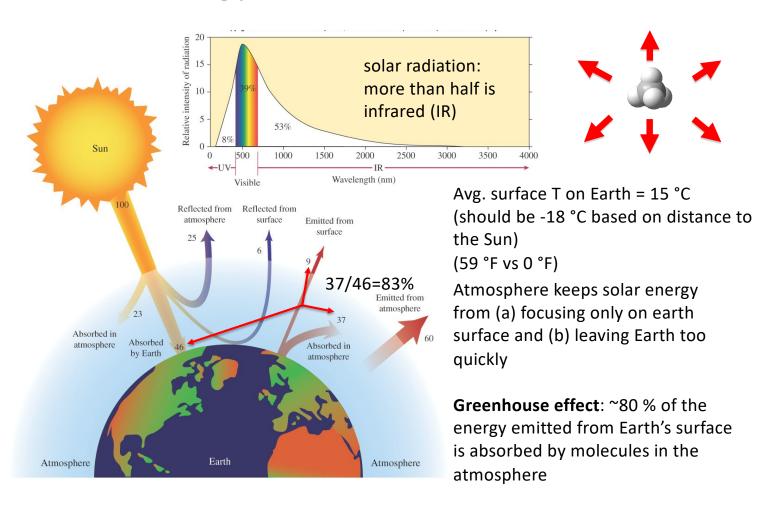
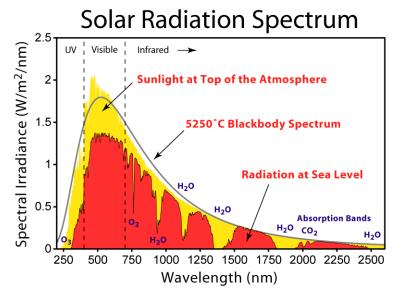
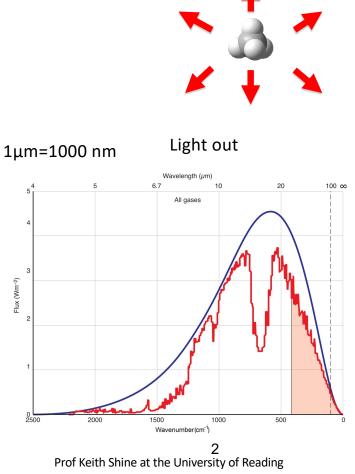
#### Solar Energy Balance



### Greenhouse effect, Solar Spectrum

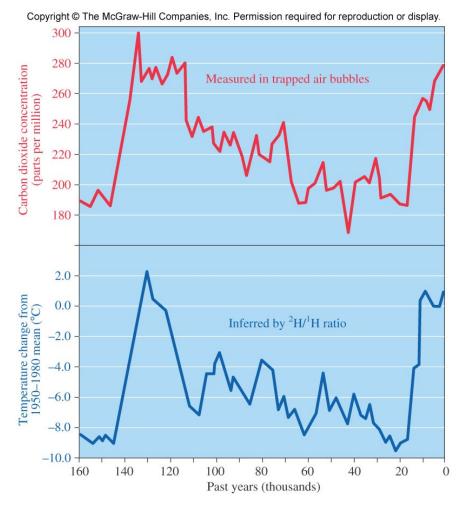


Light in



# Correlation Between CO<sub>2</sub> Levels and Temperature

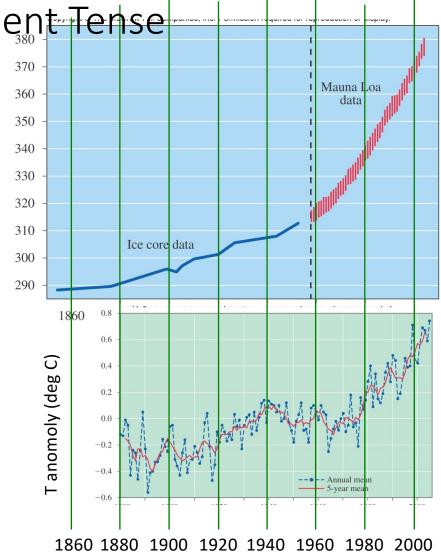
- How do we know about carbon dioxide and temperature in the past? Enter Antarctica...
- CO<sub>2</sub>
  - directly measured in gas bubbles trapped in ice
- Temperature
  - indirectly measured by looking at <sup>2</sup>H:<sup>1</sup>H ratios in the ice: water that contains <sup>2</sup>H isotopes condenses more readily than water with <sup>1</sup>H
  - the <sup>2</sup>H:<sup>1</sup>H ratio depends on temperature (beyond the scope of this course at this time)
- The CO<sub>2</sub> and T data appear to be correlated



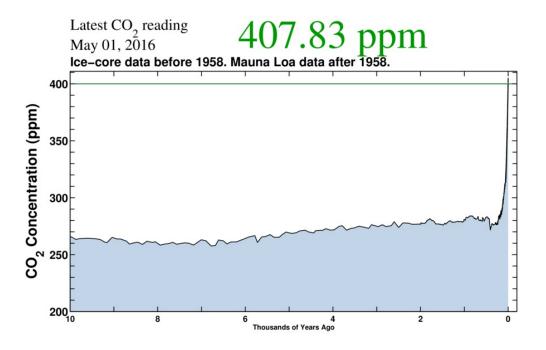
[CO<sub>2</sub>] and T: Present Tense

 Greenhouse effect absorption of heat radiation by atmospheric gases

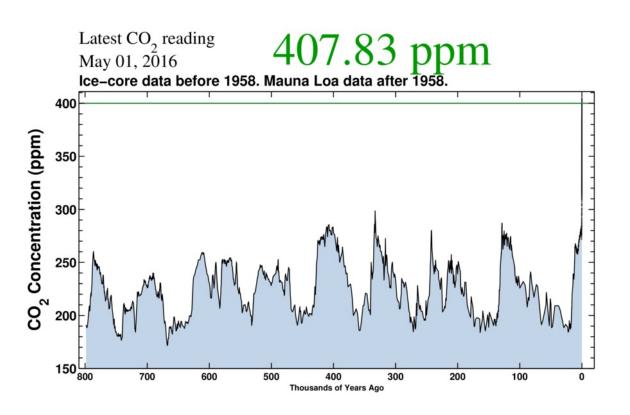
- 80% of the energy absorbed and then re-emitted by the Earth is gobbled up by the atmosphere
- represents a steady state condition
- Enhanced greenhouse effect—absorption of heat beyond the 80%
- We are currently involved in an interesting and unprecedented (for humans) experiment: how will the Earth respond to [CO<sub>2</sub>] > 400 ppm?



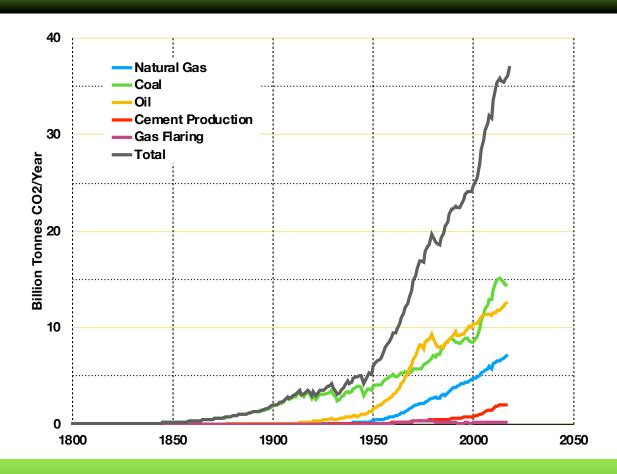
#### CO<sub>2</sub> Concentrations



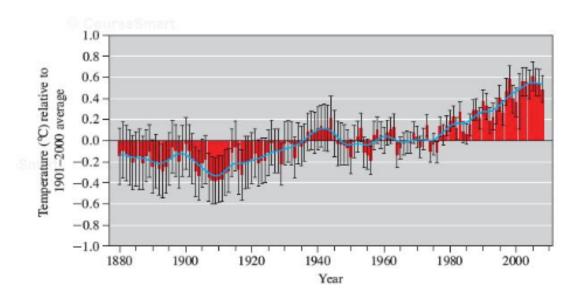
#### CO<sub>2</sub> Concentrations



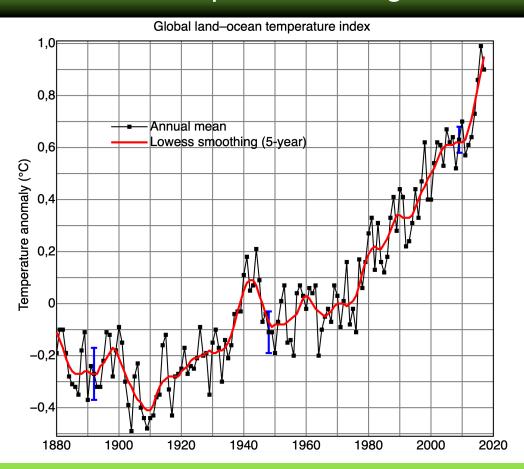
#### CO<sub>2</sub> from Fossil Fuels



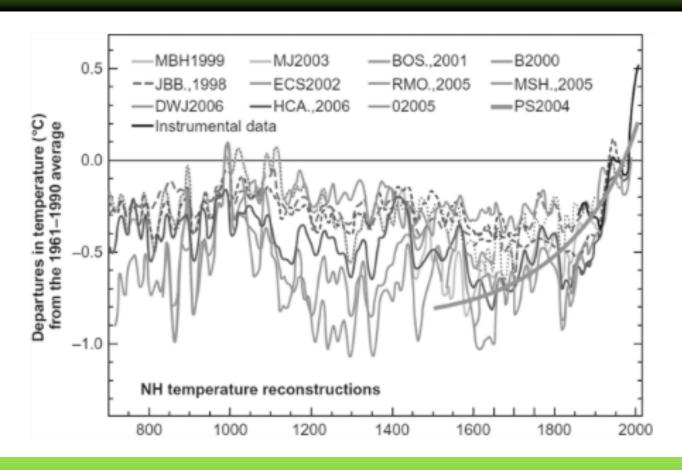
#### Land Temperature Changes



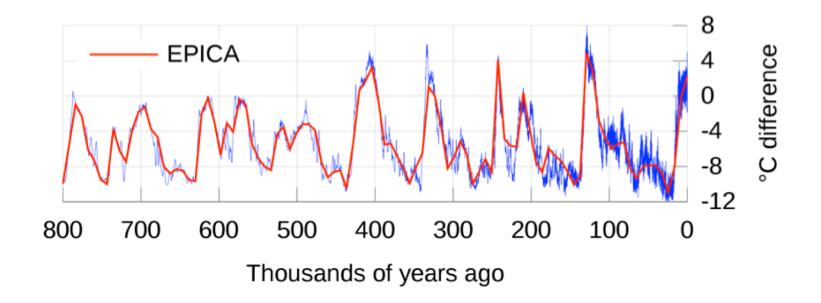
#### Land Temperature Changes



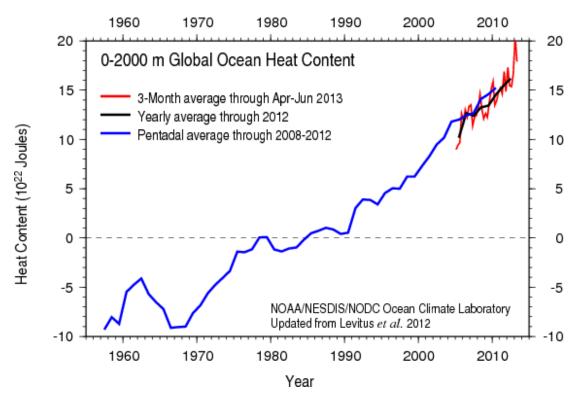
#### The "Hockey Stick"



#### Long Term Temperature Record

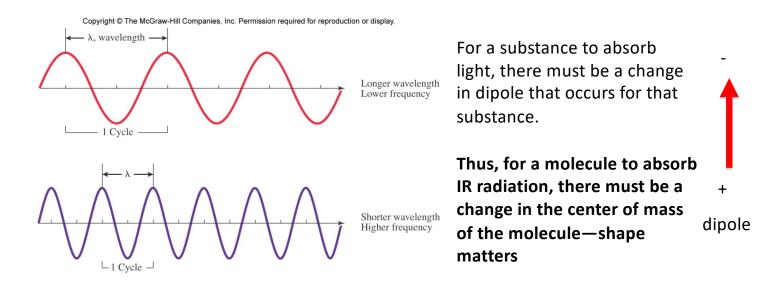


#### Ocean Heat Changes



https://www.youtube.com/watch?v=047vmL6Q\_4g

#### Light Absorption Requirements



Atmospheric gases: N<sub>2</sub> and O<sub>2</sub> don't absorb IR light, but CO<sub>2</sub> and H<sub>2</sub>O do...

N<sub>2</sub> and O<sub>2</sub> are *not* greenhouse gases, but CO<sub>2</sub> and H<sub>2</sub>O are...

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Table 1.2	Typical Composition of Inhaled and Exhaled Air	
Substance	Inhaled Air (%)	Exhaled Air (%)
Nitrogen	78.0	75.0
Oxygen	21.0	16.0
Argon	0.9	0.9
Carbon dioxide	0.04	4.0
Water vapor	0.0	4.0

### Determining Molecular Shapes Using Steric Numbers

#### • Basic procedure:

- 1. Determine # outer/valence electrons for each atom (Unit 3.2)
- 2. Arrange outer/valence electrons so each atom has noble gas configuration (Unit 3.2)
- 3. Electrons repel (but are attracted to protons) so want to be as far apart as possible—think 3-dimensionally



- if steric number (SN) = 2 (2 pairs or bonds): think linear
- if SN = 3 (3 pairs or bonds): think trigonal planar
- if SN = 4 (4 pairs or bonds): think tetrahedral
- if SN = 5 (5 pairs or bonds): think trigonal bipyramidal
- if SN = 6 (6 pairs or bonds): think octahedral

 Remember that (when asked on an exam) the molecule's **shape** depends *only* on the positions of atoms, not (lone pair) electrons



$$SN = 3$$



$$SN = 4$$



$$SN = 5$$



$$SN = 6$$

#### Practice Drawing Molecules

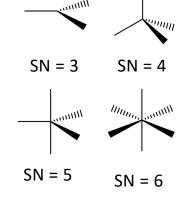
#### Examples to try:

- 1. O<sub>3</sub> (ozone)
- 2. CF<sub>2</sub>Cl<sub>2</sub> freon 12 (CFC-12)
- 3. CO<sub>3</sub><sup>2-</sup> (carbonate)
- 4. CH<sub>3</sub>SH (methane thiol)
- 5. C<sub>2</sub>H<sub>4</sub> (ethylene)
- 6. C<sub>2</sub>H<sub>6</sub>O (ethanol or dimethyl ether)
- 7.  $NO_3^-$  (nitrate)
- 8. SF<sub>6</sub> (sulfur hexafluoride)

### ,

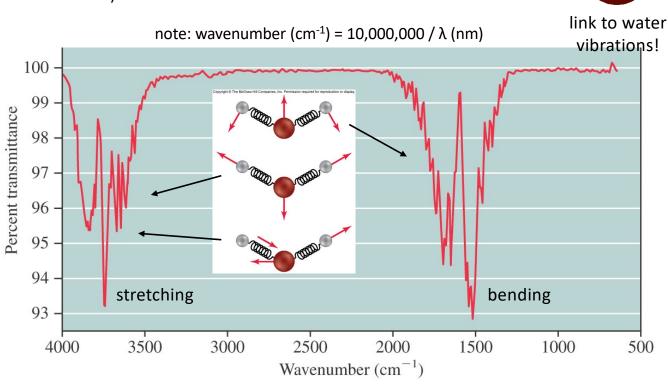
#### • Basic procedure:

- 1. Determine # outer/valence electrons for each atom (Unit 3.2)
- 2. Arrange outer/valence electrons so each atom has noble gas configuration (Unit 3.2)
- 3. Electrons repel (but are attracted to protons) so want to be as far apart as possible—think 3-D
- The molecule's **shape** depends *only* on the positions of atoms, not (lone pair) e

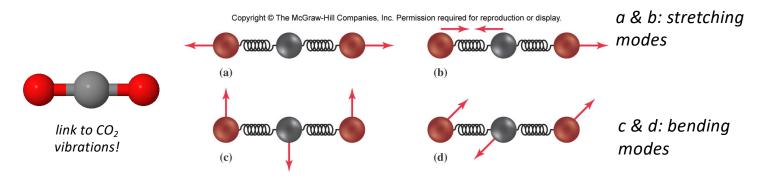


## Vibrational Modes and IR Spectrum for Water

<u>Infrared spectroscopy</u>: shine IR light (heat) onto a substance, record what energies of light are absorbed (transmittance decreases when light is absorbed)

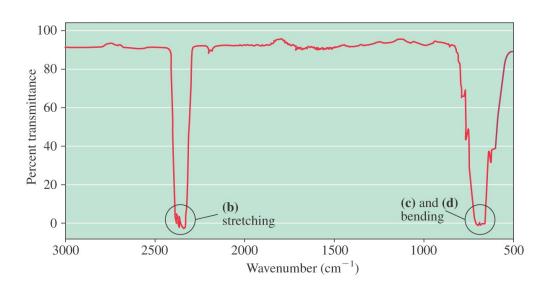


# Vibrational Modes for Carbon Dioxide and Infrared Spectrum



Which of these vibrational modes can be turned on by the absorption of IR photons?

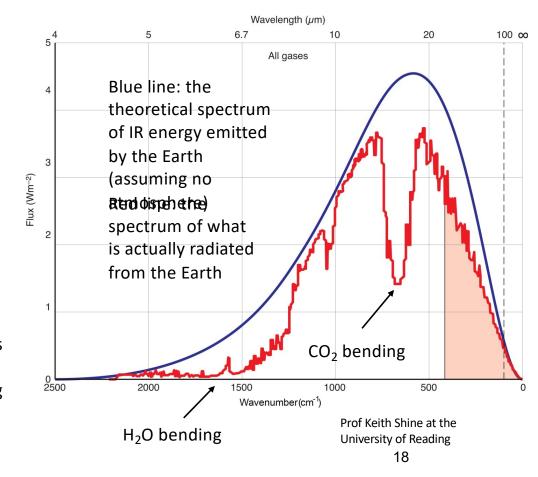
(need change in center of mass of molecule)



## Why is CO<sub>2</sub> Important for Global Warming?

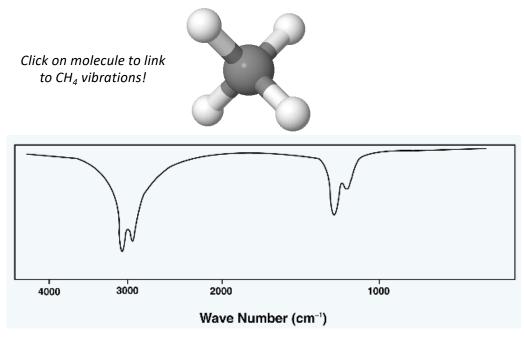
It's difficult to imagine a molecule better suited to soaking up the IR photons radiating from the Earth than carbon dioxide:

Note 900-1250 cm<sup>-1</sup> range: most of this radiation escapes into space—if a gas absorbs in this range it has greater global warming potential...



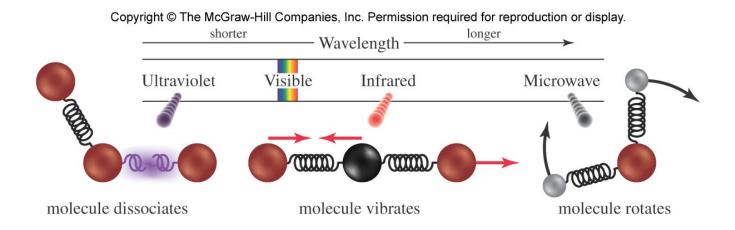
#### Methane

Is methane a greenhouse gas? If so, it needs to show vibrations that change its center of mass...



Also, the fact that there are absorptions of IR energy (the lowered transmittances at  $^{\sim}1200$  and 3000 cm $^{-1}$ ) indicate that methane can absorb IR radiation and act as a greenhouse gas.

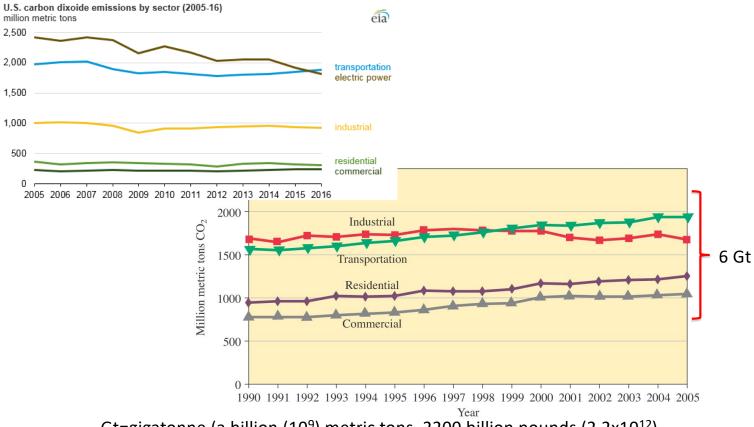
### Review of How Light Interacts with Matter



Visible—depending on the energy and substance of interest, sometimes it breaks bonds, sometimes not; vibrations almost always accompany the excitation; in some cases visible light is re-emitted by the excited substance (fluorescence and phosphorescence)

#### US Emissions of CO<sub>2</sub>

If CO<sub>2</sub> is participating in the *enhanced* greenhouse effect, it would be good to know how much is being made with respect to how much C is in the world...



Gt=gigatonne (a billion (109) metric tons, 2200 billion pounds (2.2x1012)

#### Carbon Emissions During Industrial Times

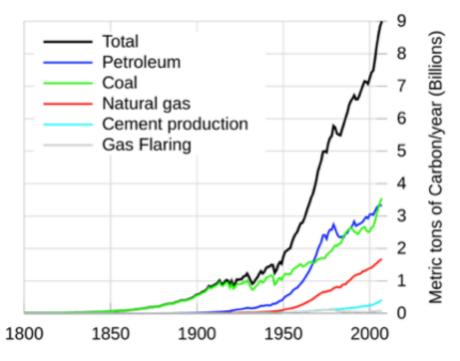


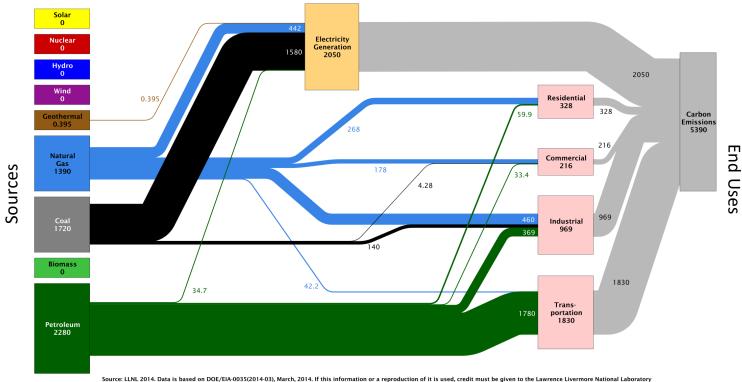
Image by Mak Thorpe, Autopilot/CC BY-SA 3.0

FIGURE 6.18 - Global carbon emissions 1800-2010

### A Different Look at US CO<sub>2</sub> Emissions (2013)

Estimated U.S. Carbon Emissions in 2013: ~5,390 Million Metric Tons



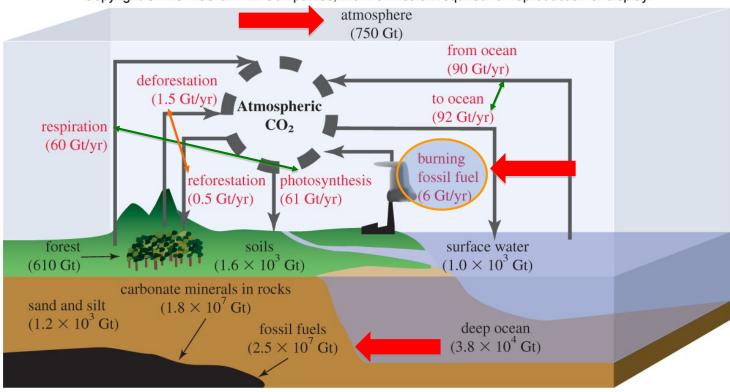


Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboraton and the Department of Energy, under whose auspices the work was performed. Carbon emissions are attributed to their physical source, and are not allocated to end use for electricity consumption in the residential, commercial, industrial and transportation sectors. Petroleum consumption in the electric power sector includes the non-renewable portion of municipal solid waste. Combustition of biologically derived fuels is assumed to have zero net carbon emissions - the lifecycle emissions associated with producing biofuels are included in commercial and industrial emissions. Totals may not equal sum of components due to independent rounding errors. LLNL-MI-01527

In millions of metric tons

### Carbon (C) Cycle

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De-reforestation 1 Gt/year Burning fossil fuels 6 Gt/year Total: 7 Gt/year Net to ocean 2 Gt/year Respiration-Photosynthesis 1 Gt/year

Total: 3 Gt/year ~3-4 Gt C/year addition to atmosphere

Gt=gigatonne (a billion metric tons (109), 2200 billion pounds (2.2x1012)