Greening Fossil Fuels

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American Chemical Society
Summer School on Green Chemistry
and Sustainable Energy
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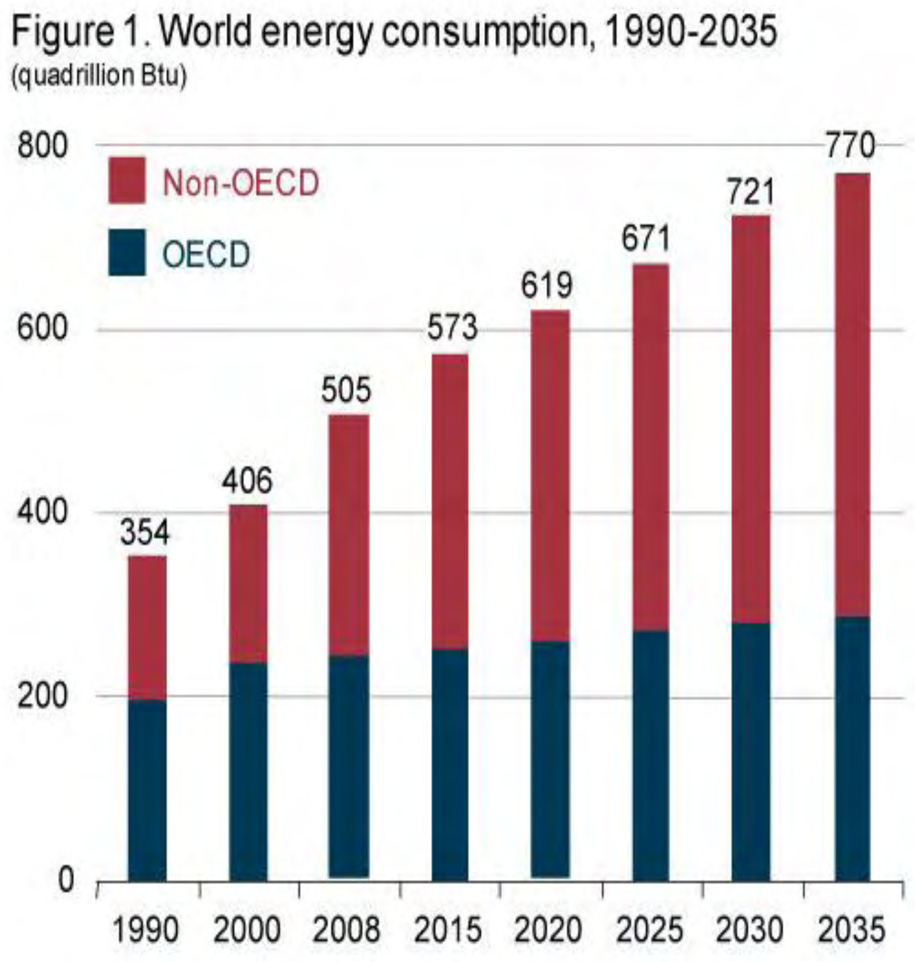
Outline

- World energy demand
- Role of fossil fuels
- NO_x, SO_2, particulate, VOCs
- CO_2
  - Global climate change
  - Carbon capture and sequestration
- Summary

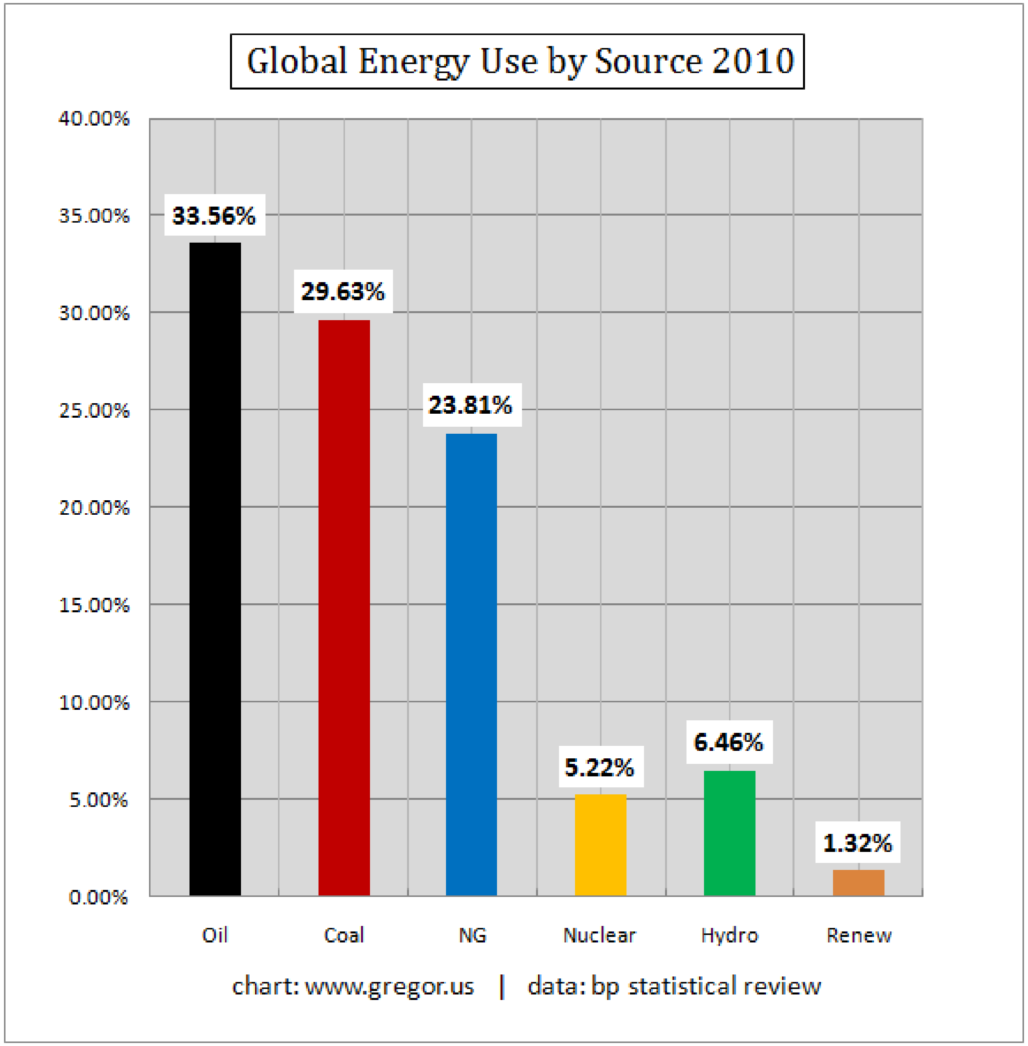
World Energy Use



Why the large increases?

Source: US Energy Information Administration: International Energy Outlook 2011.

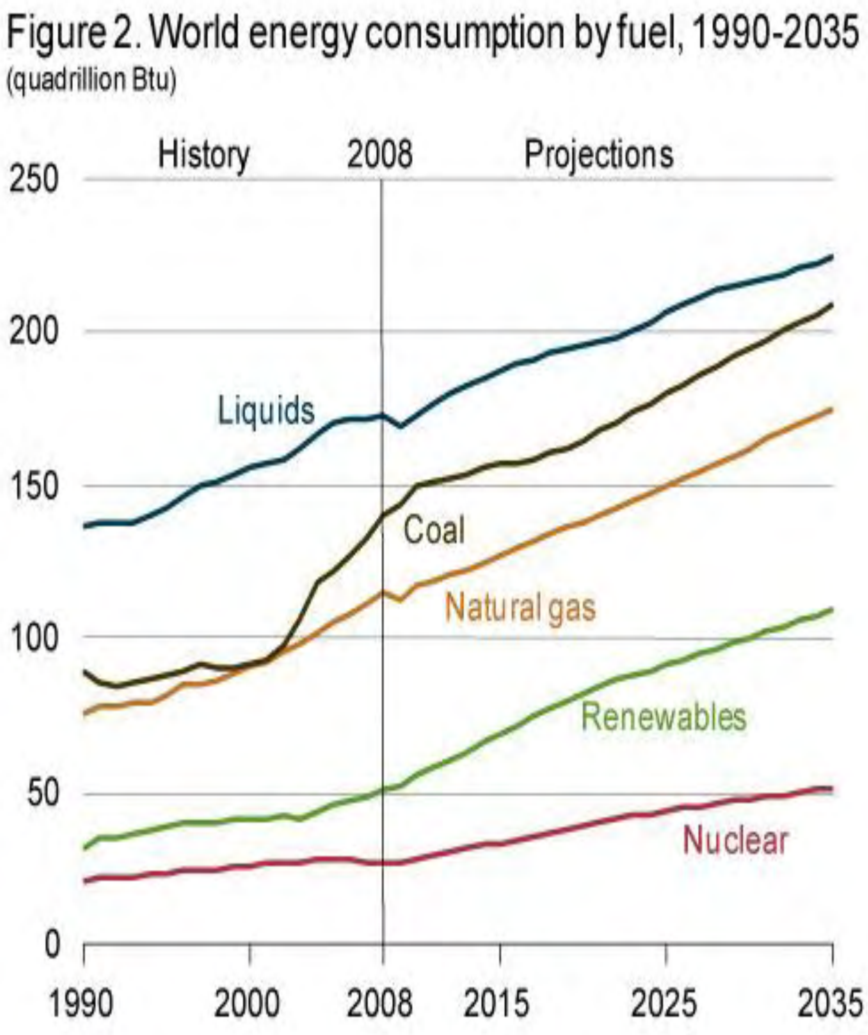
Where Do We Get Our Energy?



87%
from fossil fuels

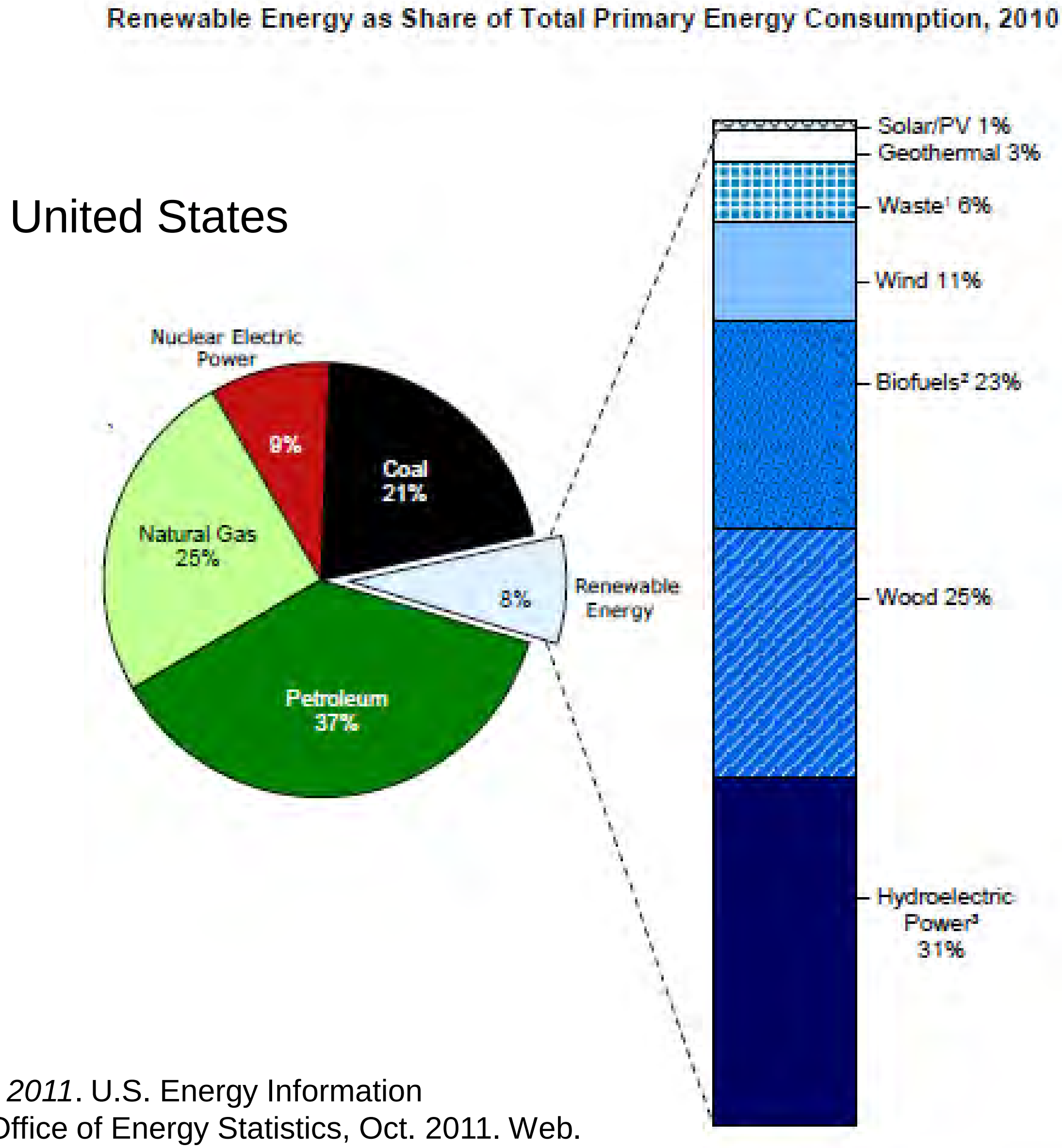
(Source: www.gregor.us via 2010 BP Statistical Review)

Where Will We Get Our Energy?



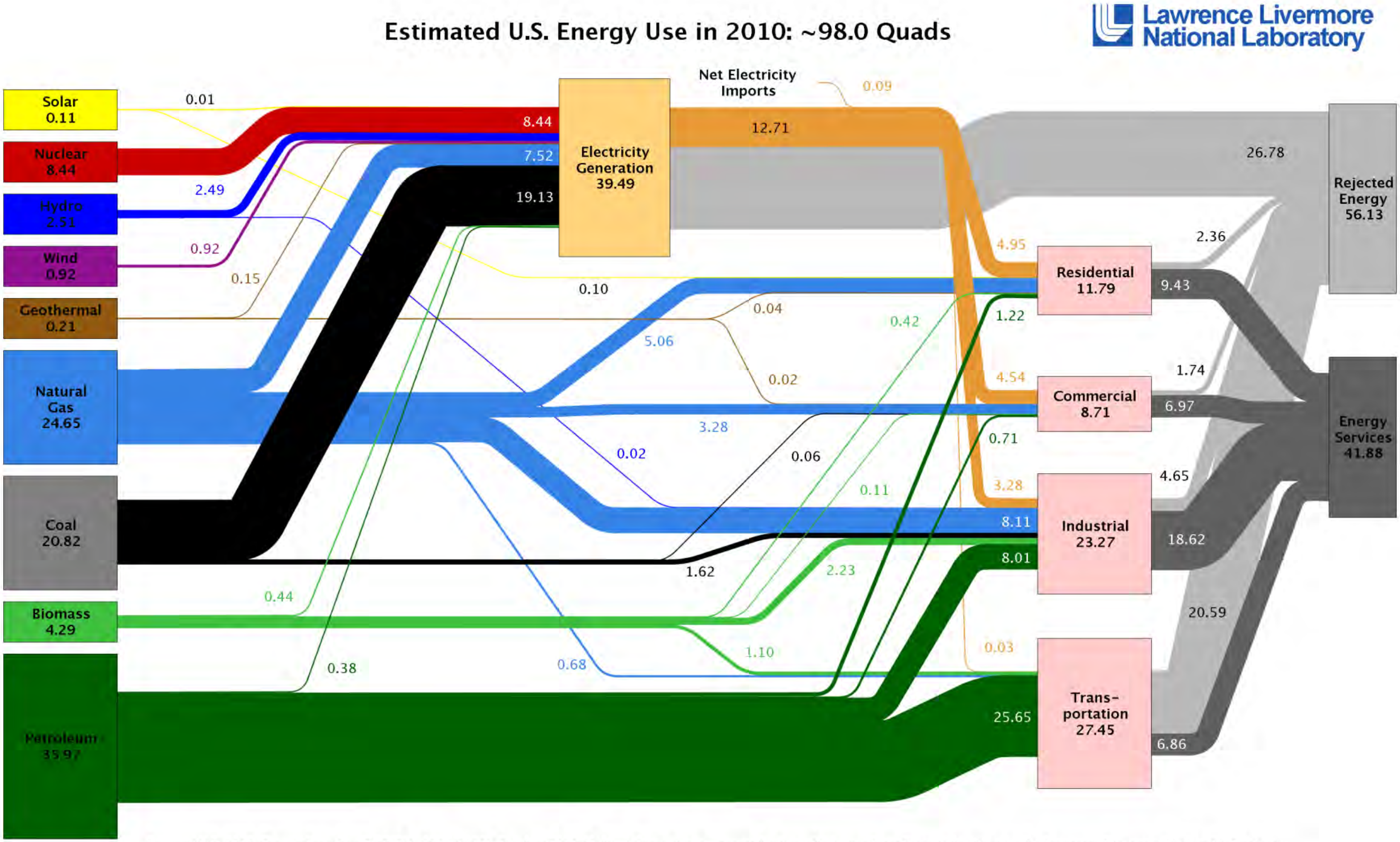
- **% from fossil fuels decrease**
- **Absolute amount from fossil fuels increase**

Where Do We Get Our Energy?



Energy Perspectives 2011. U.S. Energy Information Administration, Office of Energy Statistics, Oct. 2011. Web.

What do We Use it For?



Source: LLNL 2011. Data is based on DOE/EIA-0384(2010), October 2011. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for hydro, wind, solar and geothermal in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." (see EIA report for explanation of change to geothermal in 2010). The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

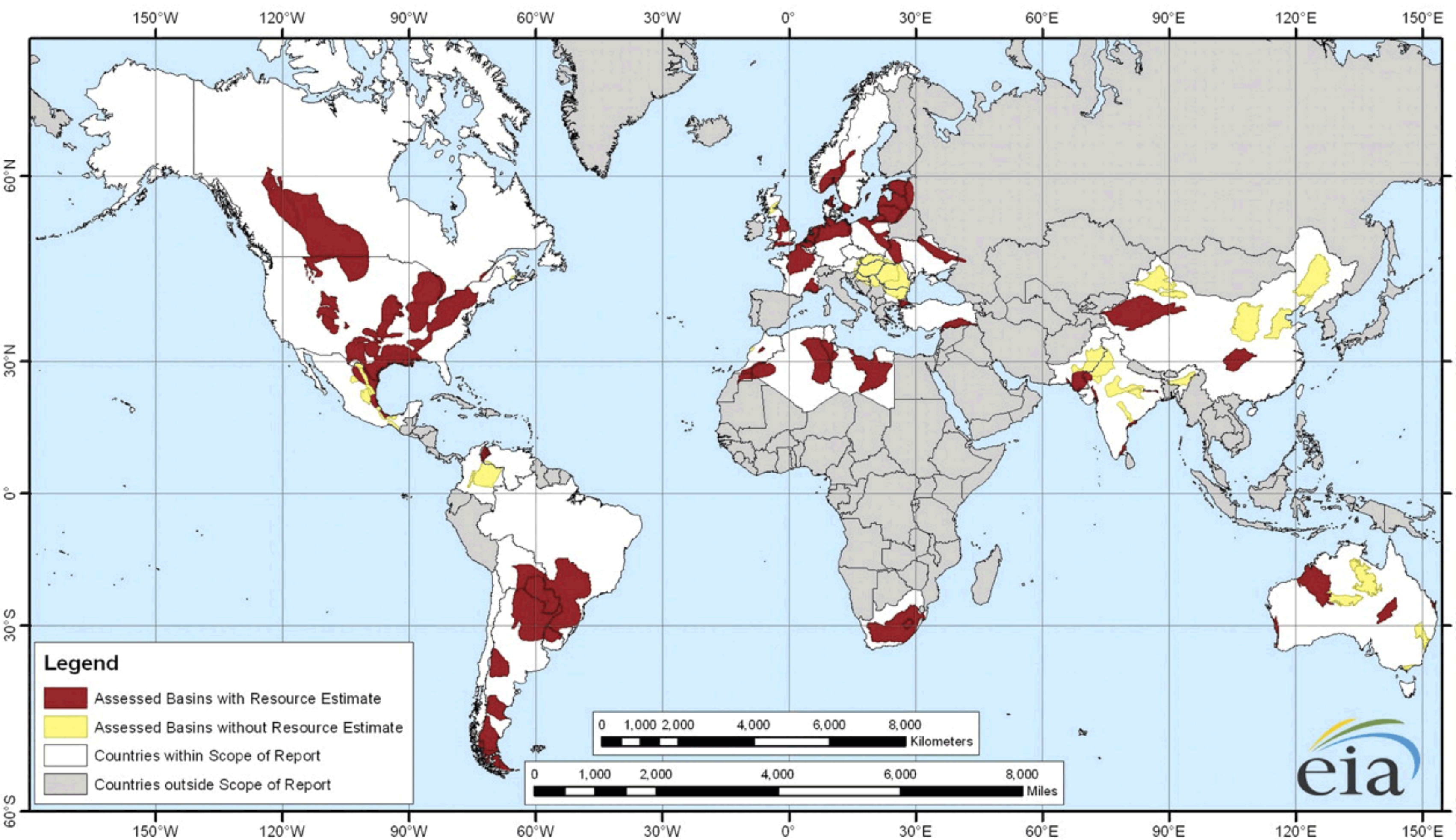
https://flowcharts.llnl.gov/content/energy/energy_archive/energy_flow_2010/LLNLUSEnergy2010.png

Role of Fossil Fuels

- Fossil fuels > 85% of primary energy consumption
- Coal ~ 50% of electricity
- Vigorous growth in renewables (wind, solar, cellulosic biomass) will require many decades before making significant contribution to primary needs
- U.S. has abundant reserves of coal and natural gas
- Will continue to use fossil fuels
- Need to use them responsibly (SO_2, NO_x, particulate, and CO_2)

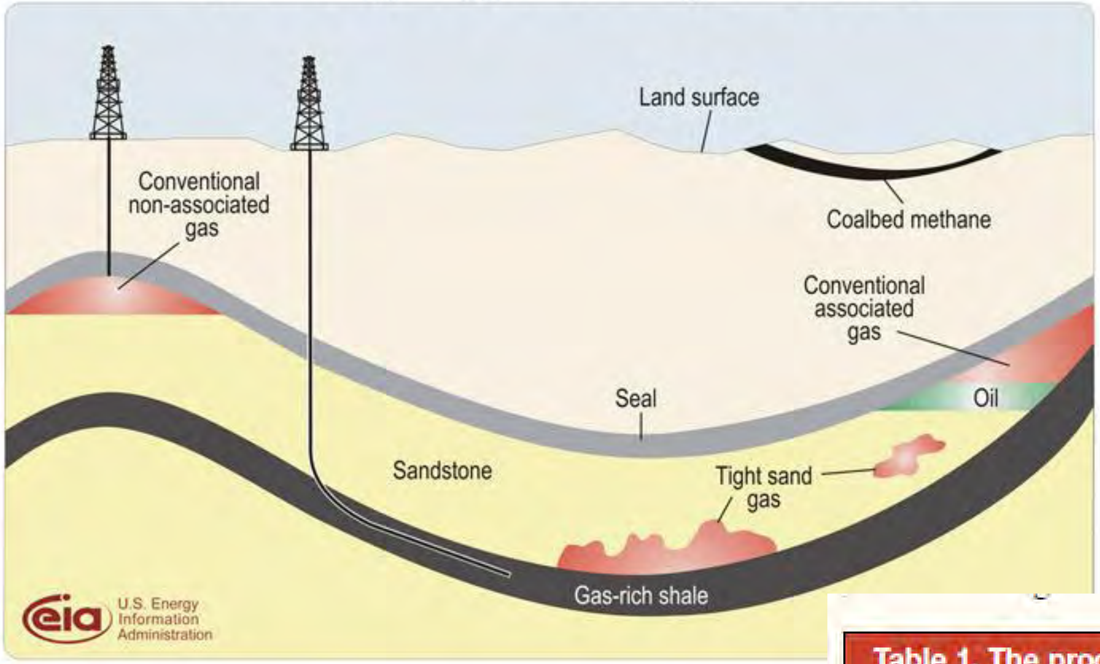
Shale Gas Resources

Natural gas found trapped in shale formations



Shale Gas Development in US

Schematic geology of natural gas resources



- 1% of US NG production in 2000
- 23% in 2010
- 49% in 2035

Table 1. The production of shale gas has increased natural gas supplies and driven down prices, resulting in significant savings in all sectors.

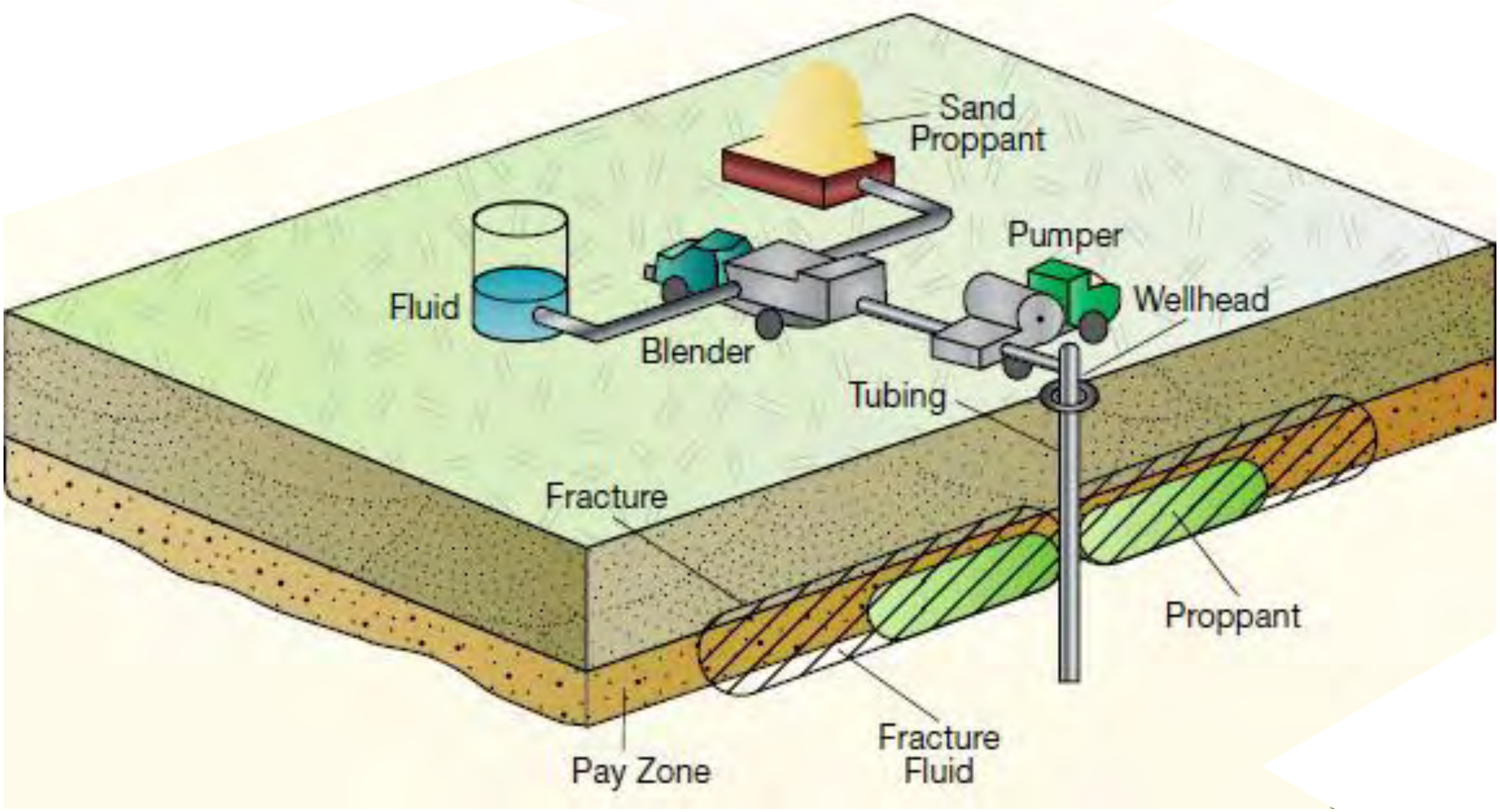
Prices, $/MMBtu*	Industrial	Power Generation	Commercial	Residential
2008 Prices	9.65	9.26	12.23	13.89
2011 Prices	5.02	4.87	8.86	10.80
Change	–48.0%	–47.4%	–27.6%	–22.2%
Sector Savings, $ billion	$31.3	$33.4	$10.7	$14.7

* per million Btu

Source: GTI analysis of DOE-EIA data.

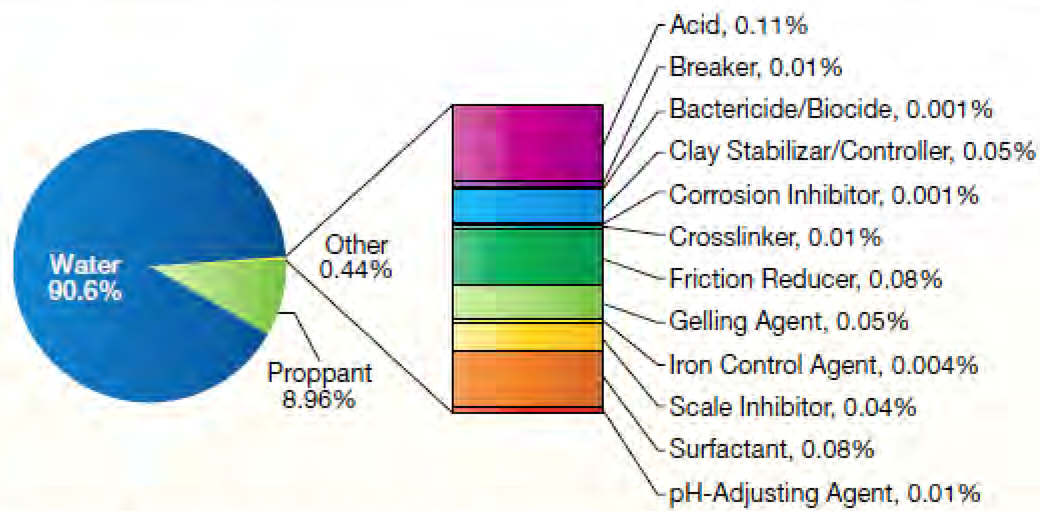
CEP, August 2012

Production of NG from Shale



CEP, August 2012

Production of NG from Shale



▲ **Figure 5.** Hydraulic fracture fluids typically consist of about 90% water, about 9% propping agent, and less than 1% functional additives.

Table 2. Most fracture fluid additives are common substances encountered in daily life.

Type of Additive	Function Performed	Typical Products	Common Use
Biocide	Kills bacteria	Glutaraldehyde	Dental disinfectant
Breaker	Reduces fluid viscosity	Ammonium persulfate	Hair bleach
Buffer	Controls the pH	Sodium bicarbonte	Heartburn-relief medicine
Clay stabilizer	Prevents clay swelling	Potassium chloride	Food additive
Gelling agent	Increases viscosity	Guar	Ice cream
Crosslinker	Increases viscosity	Borate salts	Laundry detergent
Friction reducer	Reduces friction	Polyacrylamide	Water and soil treatment
Iron controller	Keeps iron in solution	Citric acid	Food additive
Surfactant	Lowers surface tension	Isopropanol	Glass cleaner
Scale inhibitor	Prevents scaling	Ethylene glycol	Antifreeze

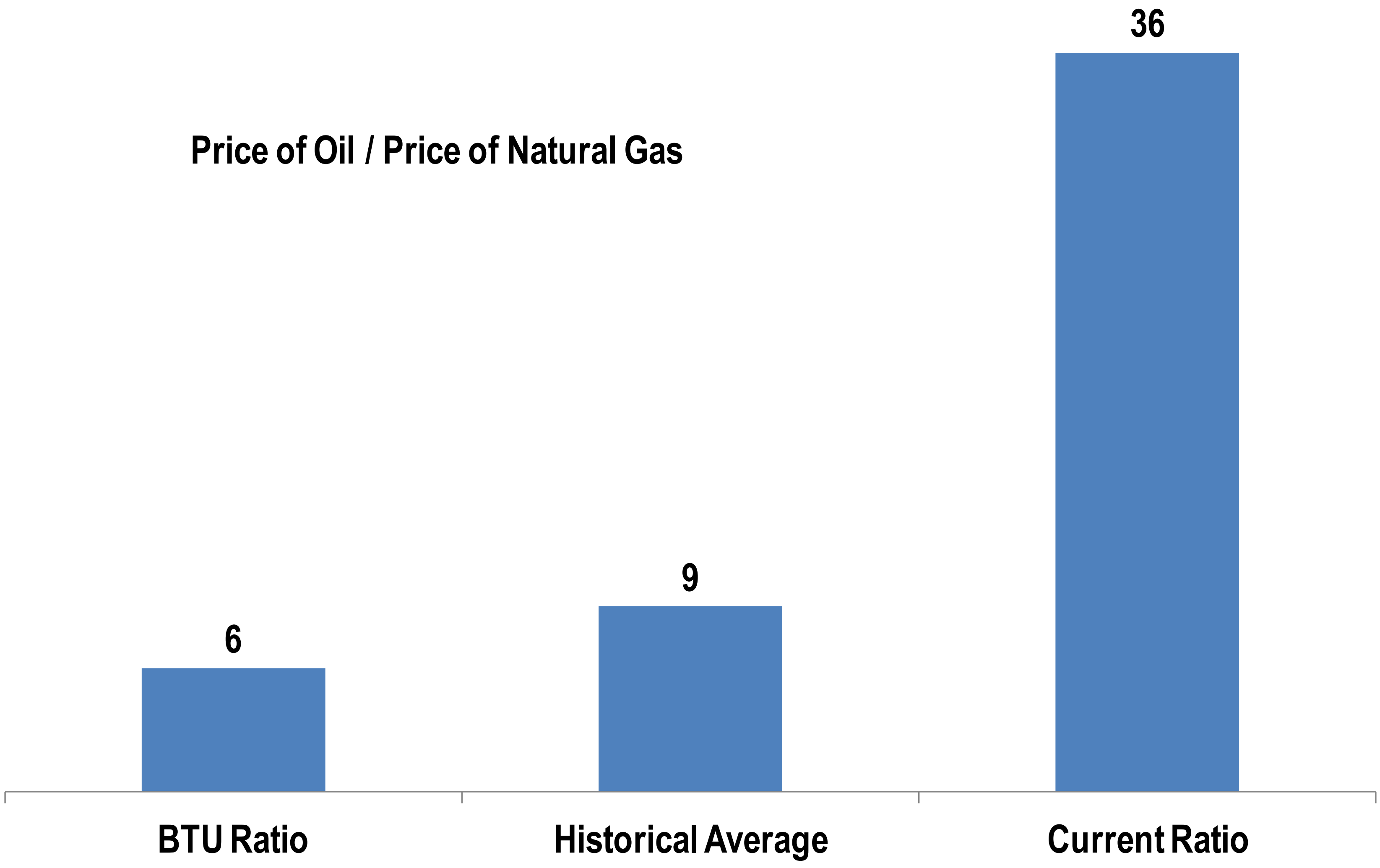
CEP, August 2012

Production of NG from Shale

- Land footprint
  - Drill multiple wells from single pad (horizontal drilling)
- Induced seismicity
  - Hydraulic fracturing creates permeability through microseismicity
  - Subsurface disposal of wastewater and produced brine
- Air emissions
  - Drilling/fracturing engines
  - Water trucks (4 million gal./800 trucks)
  - Compressor engines
  - Flaring
  - Fugitive emissions of shale gas liquids
- Water footprint
  - Water sourcing
  - Effect of roads and infrastructure on local water
  - Transportation of reuse backflow water
- Groundwater contamination
  - Complete well casing (5000 ft vs. <1000 ft)
  - Produced water
  - Treatment of surface wastewater

CEP, August 2012

Shale Gas Changing the Game



David Bem, Dow Chemical

Shale Gas LIQUIDS to Chemicals

Announced Ethylene Plants

Announced North American Ethylene Expansions			
Company	Location	Capacity (in millions/lbs)	Expected Start-Up
Dow Chemical	U.S. Gulf Coast	4,200	2014-2017
CPChem	Cedar Bayou, TX	3,300	2016-2017
Sasol	Lake Charles, LA	3,100	2016
Braskem/Idesa	Coatzacoalcos, Mexico	2,200	2015
Shell Chemical	Monaca, PA	2,000	2016+
Formosa	Point Comfort, TX	1,760	2016
LyondellBasell	Channelview & LaPorte, TX	1,350	2012-2013
OxyChem	Ingleside, TX	1,100	2015+
Dow Chemical	Hahnville, LA	800	4Q 2012
Williams	Geismar, LA	600	3Q 2013
Nova Chemical	Sarnia, ON	500	2014+
Westlake	Lake Charles, LA	230	2012
Ineos	Chocolate Bayou, TX	230	2013
Indorama	U.S. Gulf Coast	TBD	2016+
Total		21,370+	
Source: CW research, company reports.			

Ref: Chem Week, March 26, 2012

Announcements always exceed actual construction

Current NA ethylene capacity is about 32 million tpa

9.7 million tpa
Requires 10.4 million tpa ethane (theoretical for ethane feed only)

Projected new shale ethane is about 12 million tpa

David Bem, Dow Chemical

Emissions From Burning Fossil Fuels

- What do we use for home heating? What are the major emissions?
- What are the major emissions for transportation vehicles?
- Does it make sense to capture CO_2 from transportation vehicles?
- What are the major emissions from power plants?
  - Natural gas
  - Coal

Emissions – power plants

What are the typical emissions from a 500 MW coal fired power plant?

Coal used (tons)
CO_2 (tons)
SO_2 (tons)
NO_x (tons)
Ash (tons)
Hg (lbs)
HCs, CO from incomplete combustion too hard
Particulate too hard

Calculate it – don’t ‘look it up’

Emissions – power plants

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Particulate too hard

What information do you need from me?

Emissions – power plants

- What are typical emissions from 500 MW coal-fired power plant?
  - Assume:
    - 36 % efficiency
    - Bituminous coal (4% S, 1.5% N, 60% C, 0.17 ppm Hg, 24 MM BTU/ton, 10% ash)
    - Worse-case scenario; all S, N, Hg ends up in emissions
    - No pollution control devices
    - Low NO_x burners (no additional NO_x from N_2)
    - Running 24/7, 365
    - Basis: 1 yr
    - Complete combustion

Molecular weights	
C	12
O	16
N	14
S	32
Hg	200.6

Comparison with Union of Concerned Scientists Report using average actual values

	Our calcs	UCS
Coal used (tons)	1,730,000	1,430,000
SO_2 (tons)	138,400	10,000
NO_x (tons)	85,254	10,200
CO_2 (tons)	3,806,000	3,700,000
Ash (tons)	173,000	125,000
Hg (lbs)	588	
Particulate (tons)		500
Hydrocarbons (tons)		220
CO (tons)		720

Why do we care about SO_2 and NO_x emissions?

Why do we care about Hg emissions?

Why do we care about particulate emissions?

Why do we care about HC emissions?

What can we do to reduce our emissions?

- Improve cycle efficiency
  - reheat, cogen, combined cycle…
  - Limited by 2nd law of thermo (can't turn all heat into work)
- Alternative combustion schemes
  - Integrated gasification combined cycle (IGCC)
- Low NO_x burners
  - Thermal NO_x (N_2 from air)
  - Need to keep temperature down
  - Reduces NO_x by 50%

What can we do to reduce our emissions?

- Flue gas desulfurization
  - Expose to limestone ($CaCO_3$) to form gypsum ($CaSO_4$) and calcium sulfite ($CaSO_3$)
  - Dry systems: 70-90% removal
  - Wet systems: 95% removal
- Selective catalytic or non-catalytic reduction of NO_x (SCR or SNCR)
  - Inject ammonia ($NH_3 + NO_x = N_2 + H_2O$)
  - SNCR: 40-60% removal
  - SCR: 90% removal

What can we do to reduce our emissions?

- Electrostatic precipitators (ESP) and fabric filters (FF)
  - Both remove >99% of particulate matter
  - FF better at getting out smaller particulates
    - FF>99%
    - ESP 85-95%
  - Also remove Hg (especially FF)!
    - Dry scrubber + FF removes > 95%

CO_2

- Why do we care about CO_2 emissions?

Home ›

Santorum Denies Global Warming

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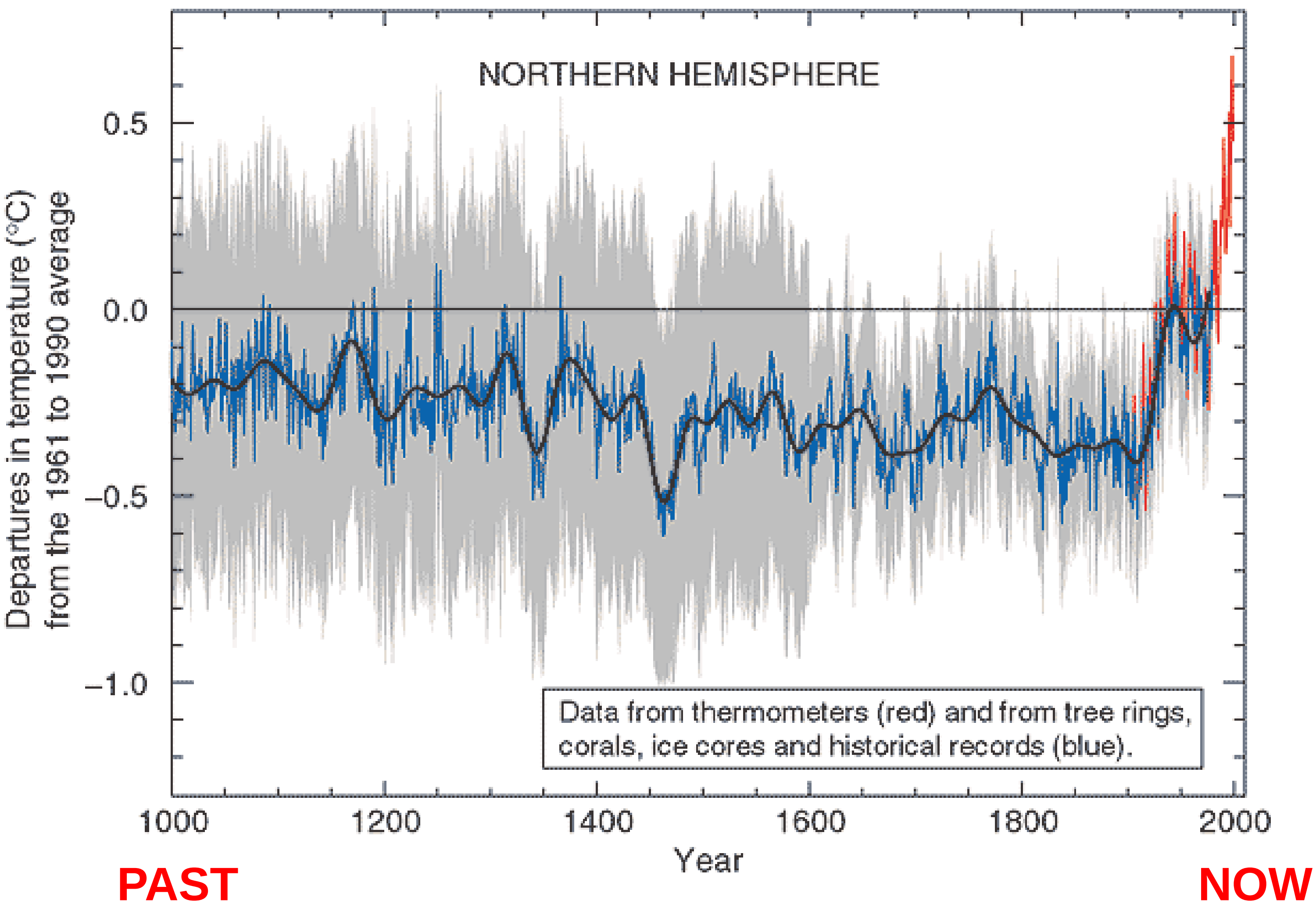
By Amitabh Pal, March 16, 2012

"I am the only one who has not bowed, and will never bow, to this liberal orthodoxy."

Even for a party that wears its anti-science label almost with pride, the GOP has recently been outdoing itself on global warming.

"The dangers of carbon dioxide? Tell that to a plant, how dangerous carbon dioxide is," presidential contender Rick Santorum said at the Gulf Coast Energy Summit in Biloxi, Mississippi, on March 12.

Historical Temperature 'Data' – Last 1000 years

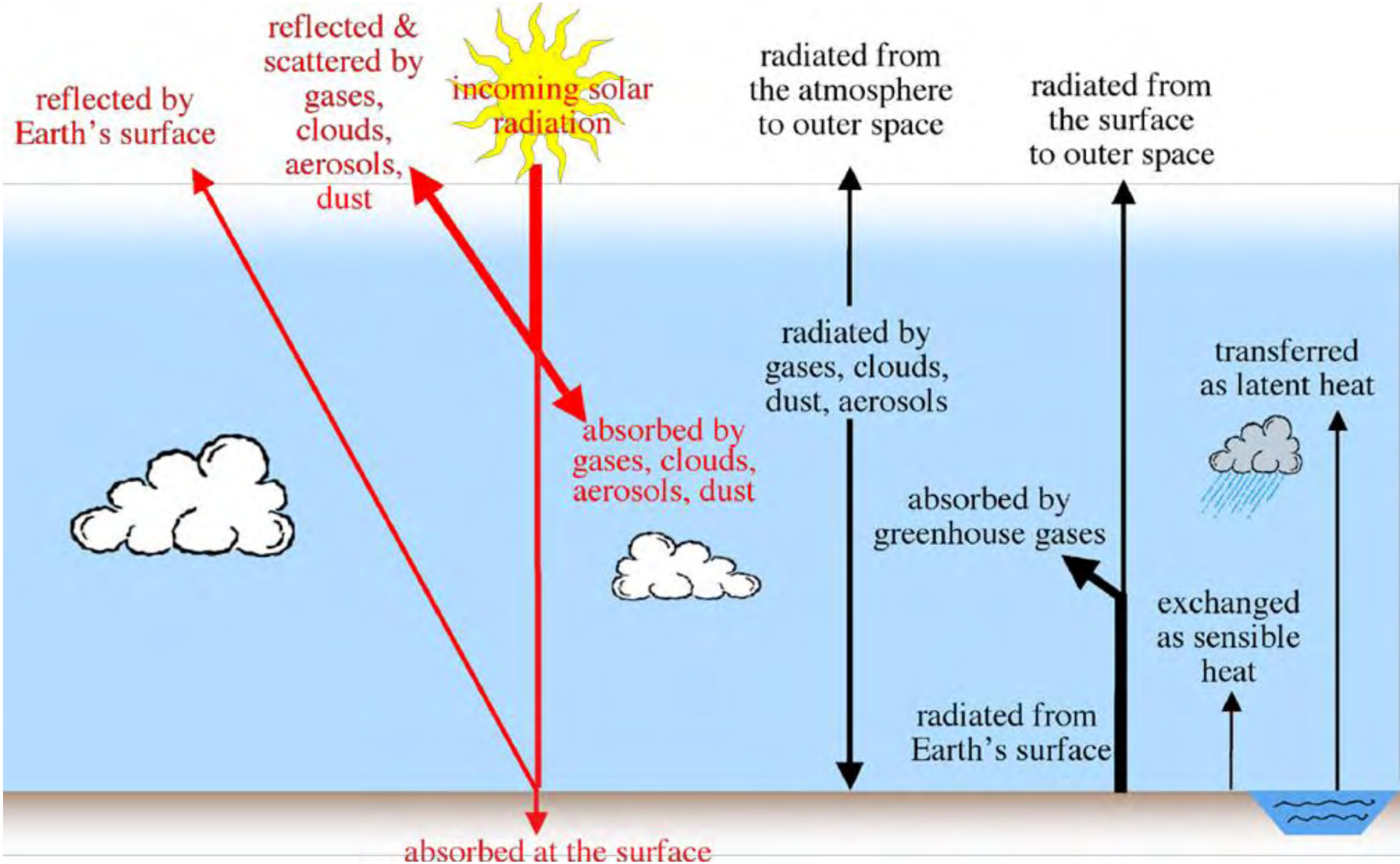


This is the famous "hockey stick" diagram of Mann, Bradley and Hughes (1998)

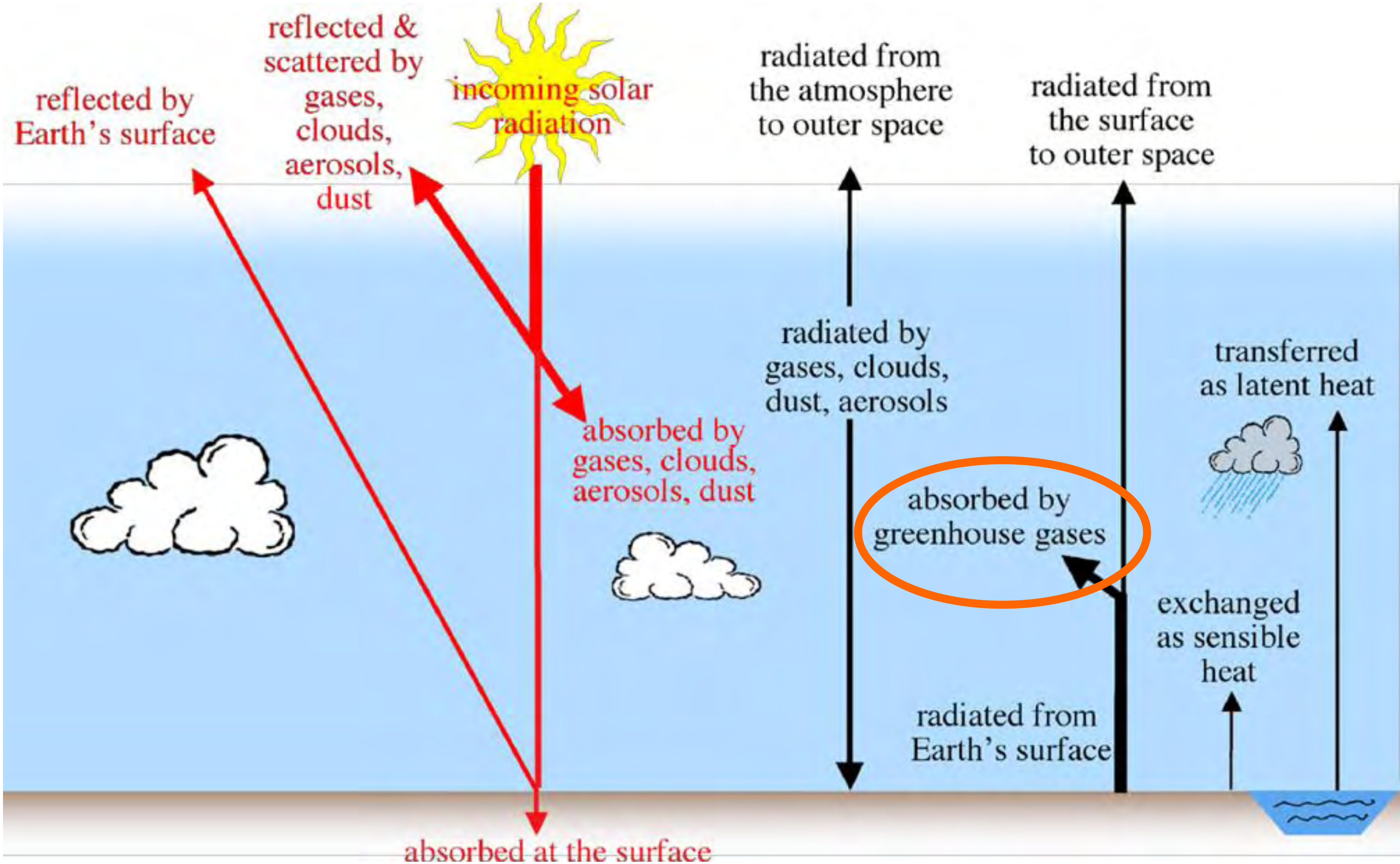
Developing a Model of Effect of Greenhouse Gases on Climate

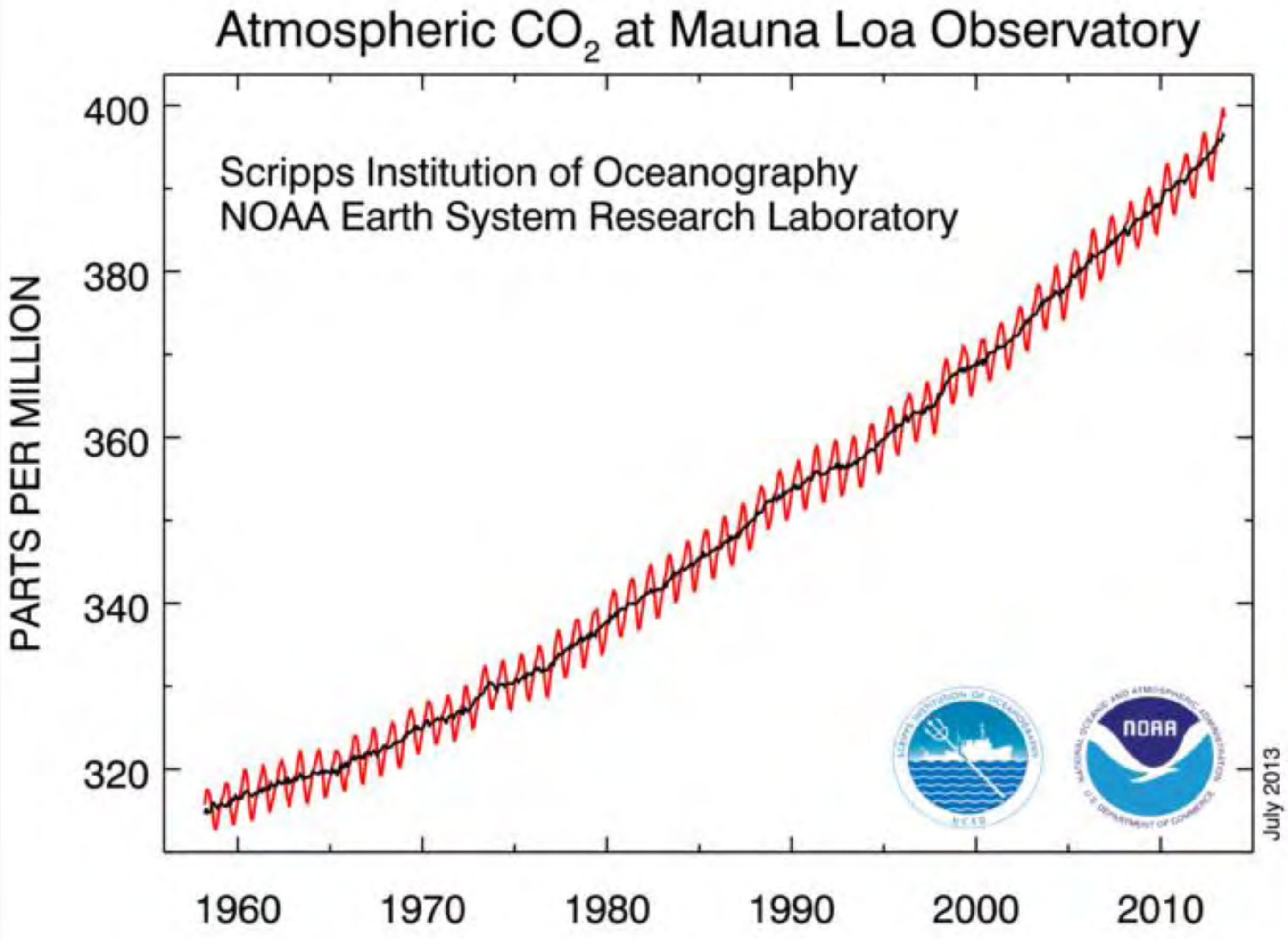
- Need energy balance on earth
- Need to know how carbon moves around in our environment

Energy Balance on the Earth



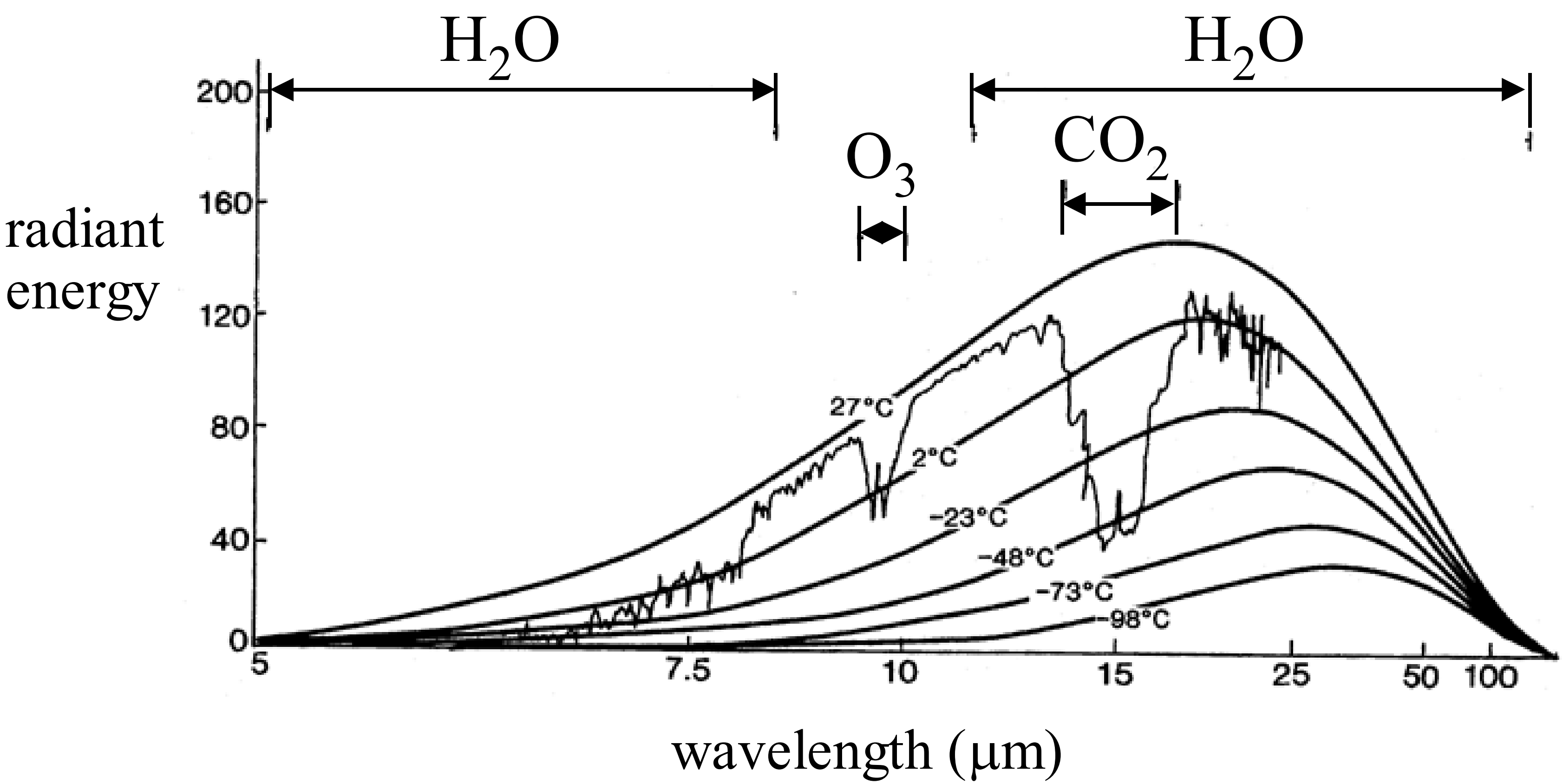
Energy Balance on the Earth



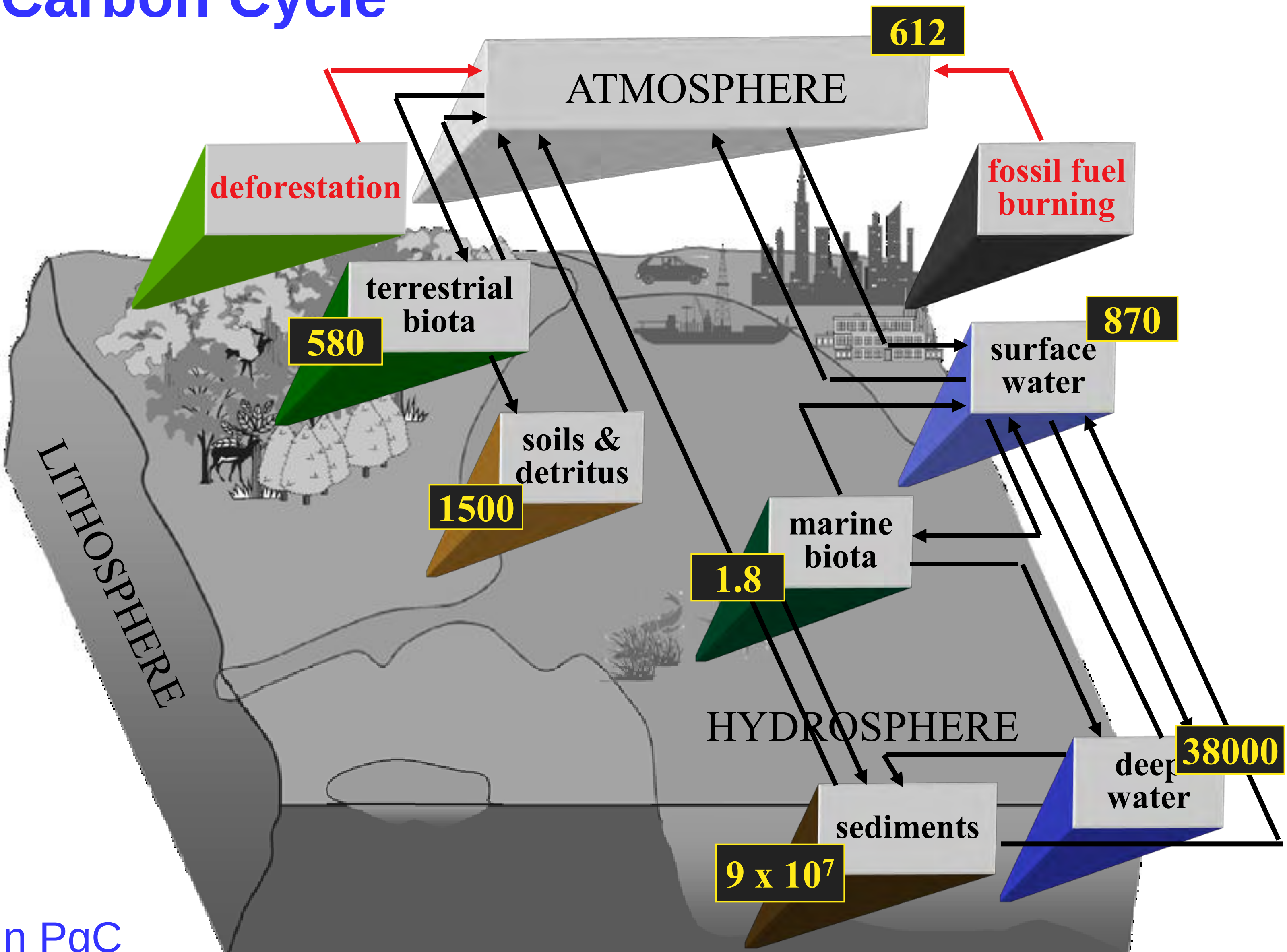


http://www.esrl.noaa.gov/gmd/ccgg/trends/

Greenhouse Gases Absorb Infrared Radiation

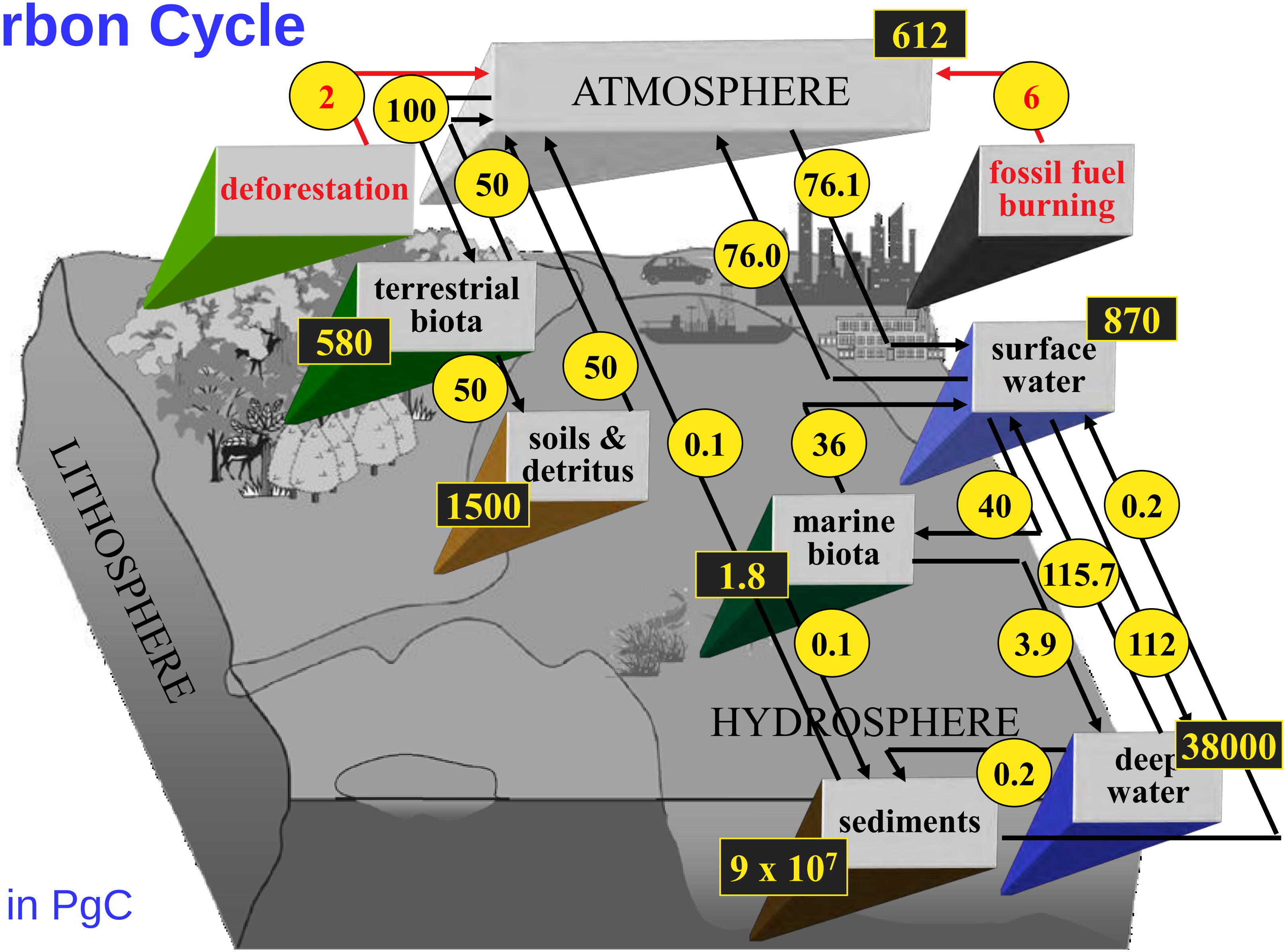


The Carbon Cycle



Amounts in PgC
(pre-industrial, ca1850)

The Carbon Cycle



Amounts in PgC

Fluxes in PgC/y

(all pre-industrial, ca1850, except disturbances are current)

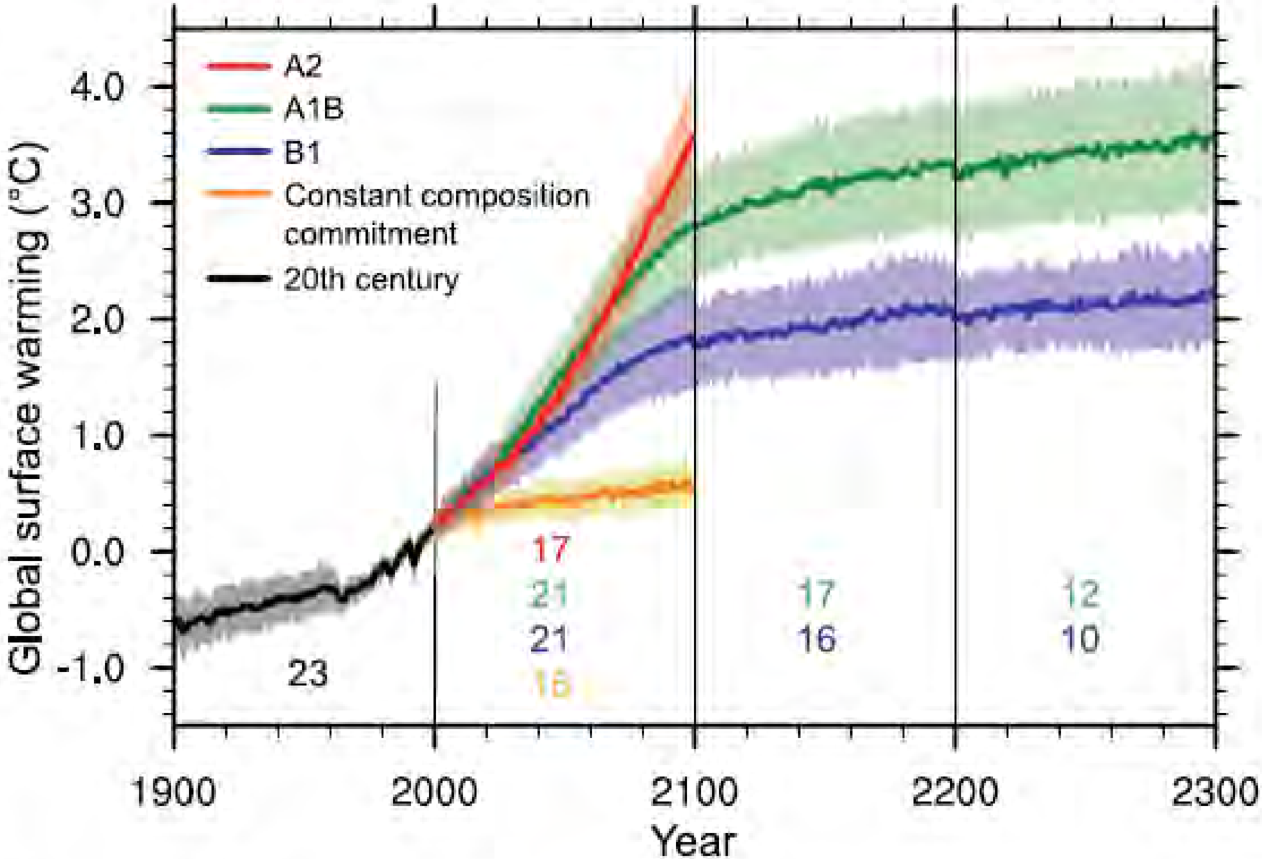


Figure 10.4. *Multi-model means of surface warming (relative to 1980–1999) for the scenarios A2, A1B and B1, shown as continuations of the 20th-century simulation. Values beyond 2100 are for the stabilisation scenarios (see Section 10.7). Linear trends from the corresponding control runs have been removed from these time series. Lines show the multi-model means, shading denotes the ±1 standard deviation range of individual model annual means. Discontinuities between different periods have no physical meaning and are caused by the fact that the number of models that have run a given scenario is different for each period and scenario, as indicated by the coloured numbers given for each period and scenario at the bottom of the panel. For the same reason, uncertainty across scenarios should not be interpreted from this figure (see Section 10.5.4.6 for uncertainty estimates).*

IPCC 2007

Observations

- CO_2 concentrations in the atmosphere are increasing
- Global temperatures are increasing
- Is one causing the other?
  - Not as simple as plotting CO_2 and temperature on same graph
  - IPCC says “very likely”
- Consequences?
  - Warming temperatures
  - Rising sea levels (expansion and melting)
- Connection with other consequences much less certain

Summary

- Meeting world energy needs is greatest challenge of this century
- Significant gains can be made in energy efficiency
- Will continue to use fossil fuels (especially coal and NG) until renewables grow to meet a significant fraction of our energy needs
- Shale gas has completely changed US energy and chemicals landscape
- Burning of fossil fuels is very likely linked to global climate change
- Need to use fossil responsibly – CO_2 capture