Lecture 6

Air Pollution Emissions

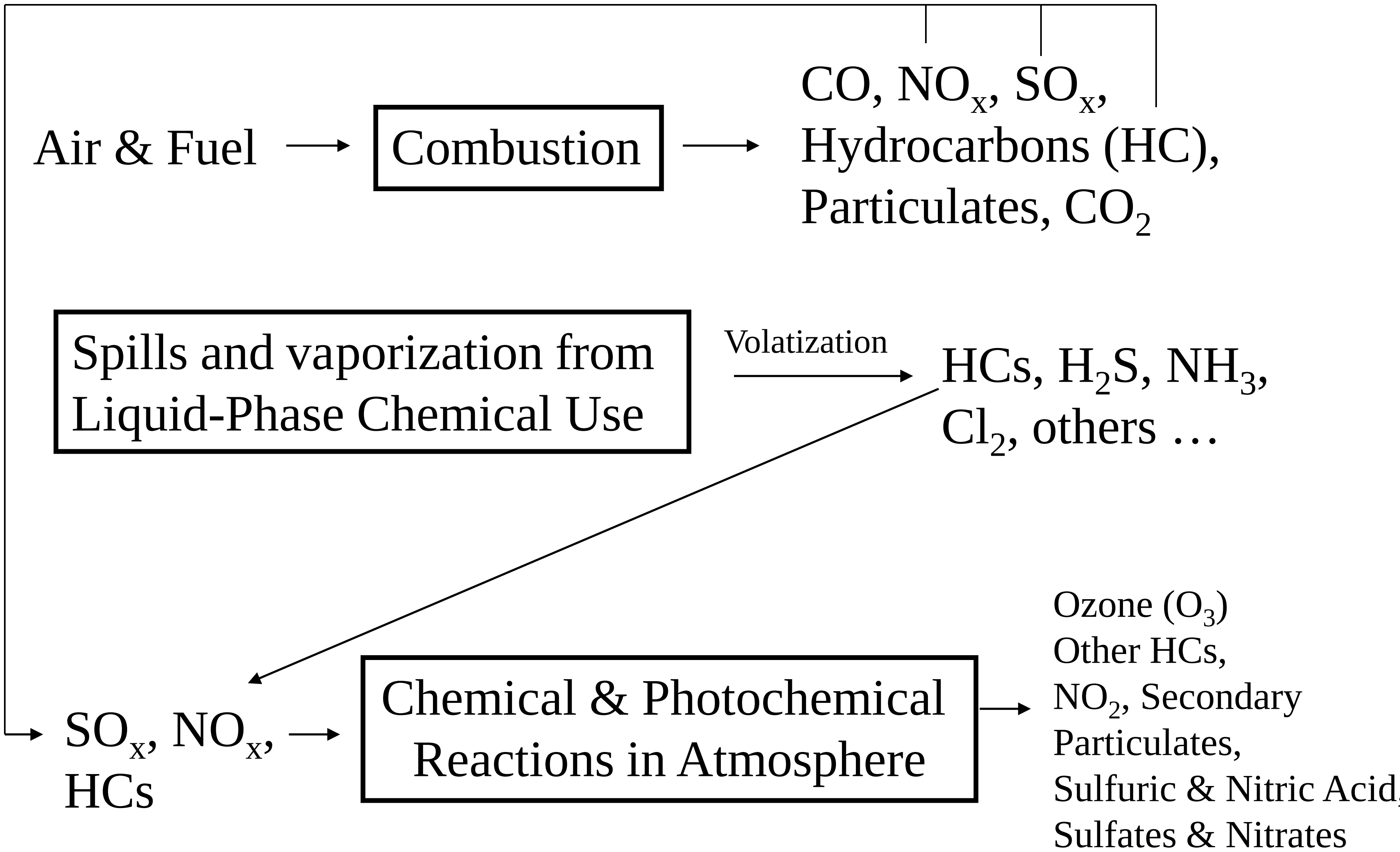
(focus mainly on combustion of carbon-based fuels)

METR 113/ENVS 113
Spring Semester 2011
April 19, 2011

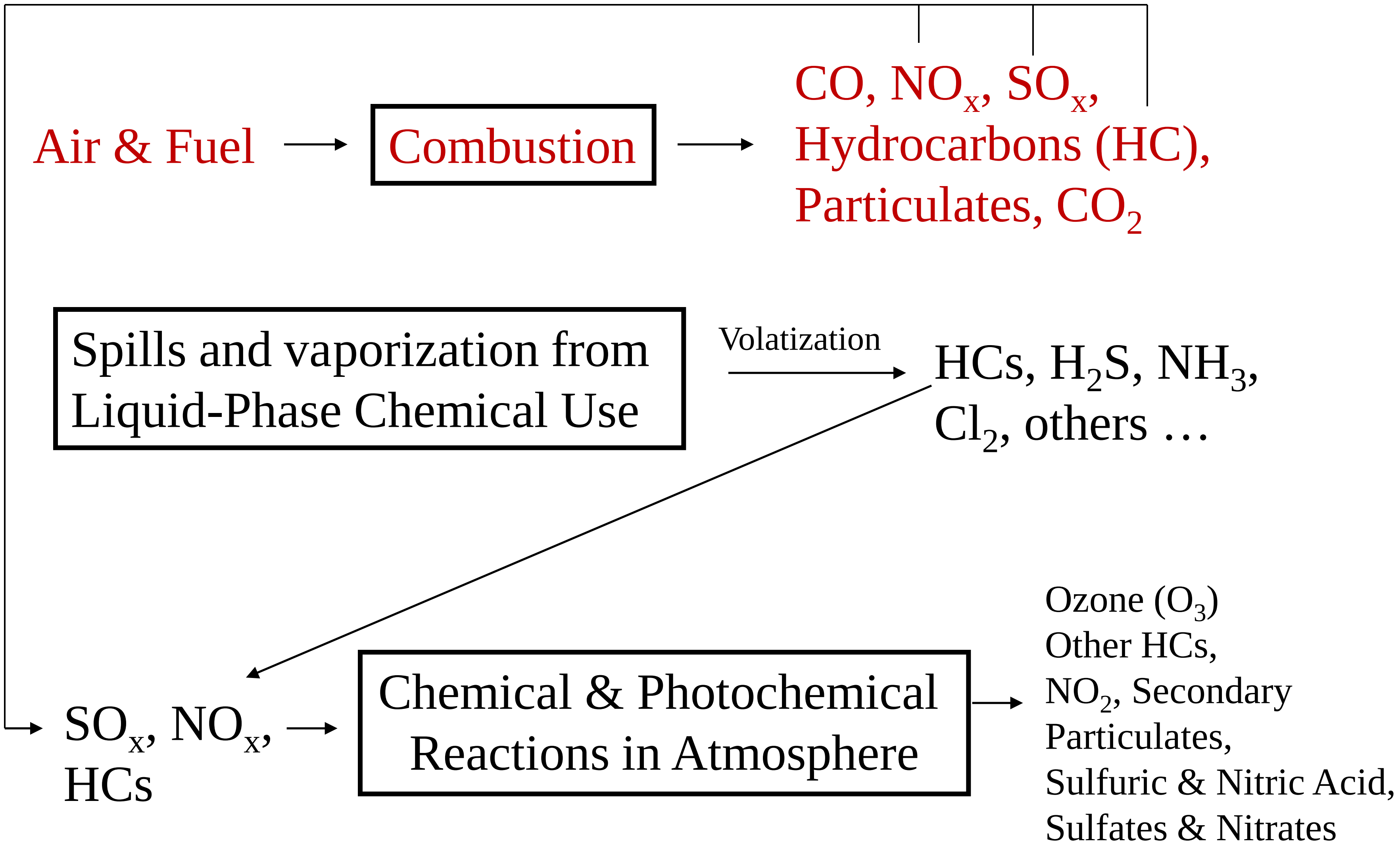
Reading …

- To be determined ..

Sources of Air Pollutants …



Focus on Combustion …



What do we mean by "combustion"?

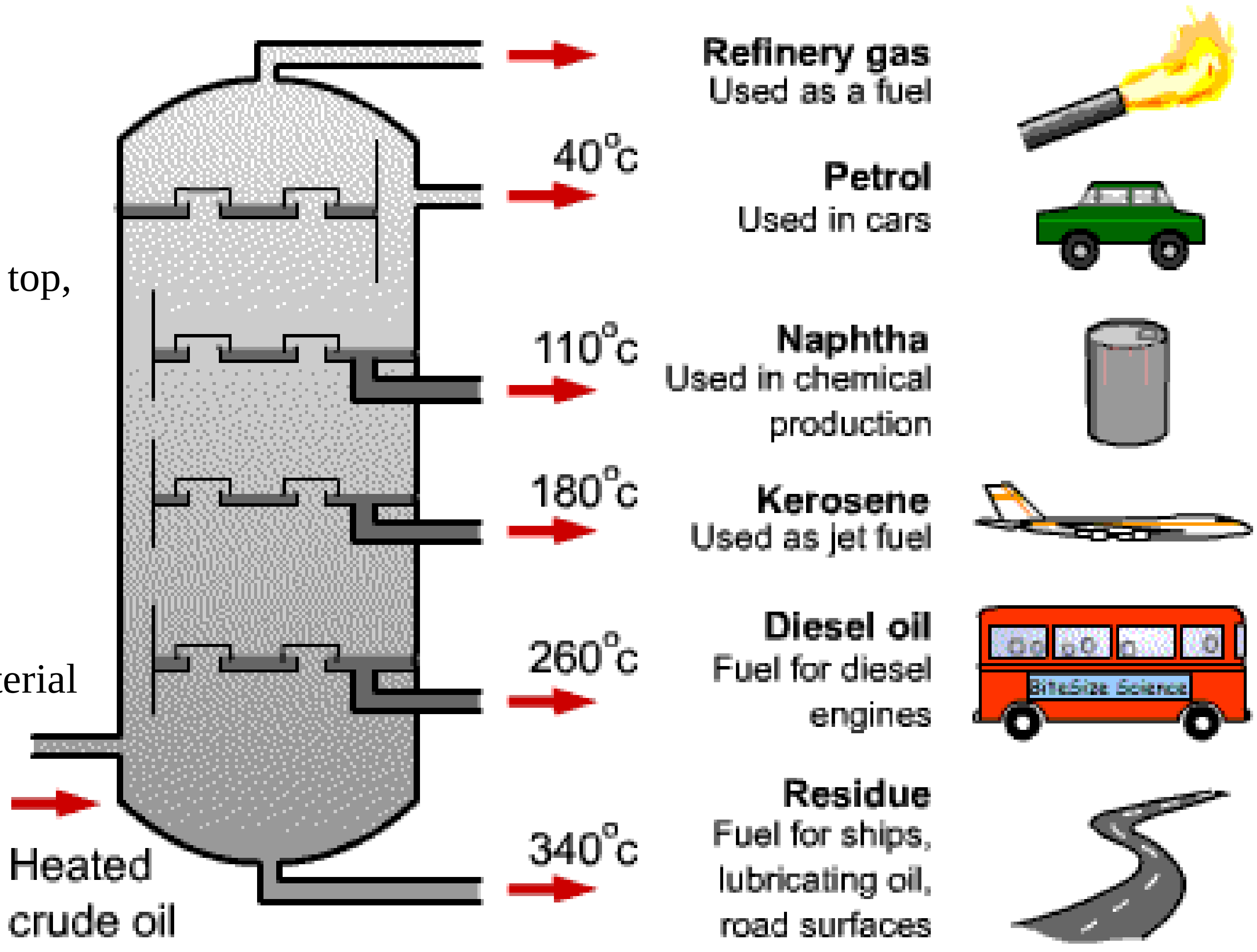
- Combustion = **burning** something
- For example …
  - Burning gasoline in automobiles
  - Burning diesel fuel in trucks
  - Burning "residual oil" (bunker fuel) in ships
  - Burning coal in power plants
  - Burning natural gas (methane, CH_4) in power plants
  - Burning wood and other biomass in wildfires & controlled burns
- Underlined "fuels" above are all carbon-based fuels
- All except wood & biomass are "fossil fuels".
- Sources of fossil fuels
  - Extraction of natural gas (methane, CH_4) from earth
  - Crude oil distillation (where crude oil is extracted from earth)

Distillation of Crude Oil

(Where lots of our fossil fuel come from …)

lighter material on top,

heavier material on bottom



“refinery gas” = natural gas

Distillation Tower in a Refinery

Emissions from Combustion

(let "fuel" below be some carbon-based fuel)

Air & Fuel → Combustion → CO_2, CO, NO_x, SO_2, Unburned HCs, Particulates

$$C_mH_n + O_2 + N_2 \rightarrow CO_2 + H_2O + \text{other products } (SO_2, NO_x, \text{Particulates, etc} \ldots)$$

Fuel (${C_mH_n}$) ***Air*** ($O_2 + N_2$) ***Products***

Notes about combustion …

- **<u>Complete Combustion</u> – all carbon and hydrogen in fuel and oxygen in air is converted to carbon dioxide (CO_2) and water vapor.**
- **<u>Incomplete Combustion</u> – some carbon/hydrogen/oxygen goes to other products (carbon monoxide, various hydrocarbon gases, black carbon/soot, etc …)**
- **Any sulfur in fuel is converted to sulfur dioxide (SO_2)**
- **Nitrogen in air is converted to nitrogen oxides (NO and NO_2)**

Clean Air vs. Combustion Gas

- Clean Air
  - Nitrogen (78%)
  - **Oxygen (21%)**
  - **Carbon Dioxide (0.03%)**
  - Others very small

- Flue Gas (released to air after combustion from smokestacks)
  - Nitrogen (78%)
  - **Oxygen (2-6%)**
  - **Carbon Dioxide (10-15%)**
  - SO_2, CO, NO_x, Particulates, HCs higher levels than clean air

Air-Fuel ratio is important …

- Complete Combustion: “just right” amount of air vs. fuel …
- Fuel “rich”: More fuel than air
- Fuel “lean”: More air than fuel
- If too rich or too lean, combustion will not occur
- Determines which types of air pollutants are formed
  - Fuel Rich: High levels of CO, particulates, unburned HCs
  - Fuel Lean: High levels of NO_x
- Other pollutants
  - SO_2 is formed as long as there is sulfur in fuel (rich or lean)
  - CO_2 is formed in either case (rich or lean). Unavoidable (!)

2008 TOYOTA SEQUIOA 5.7L V8

Smog Check Vehicle Inspection Report (VIR)

Vehicle Information

Test Date/Time: 04/23/2009 @ 11:13

Model Year:	2008	Make:	TOYOTA	Model:	SEQUOIA
License:	HH2HYGN	State:	CA	VIN:	5TDZY68A78S007553
Engine Size:	5.7 L	Type:	Truck	Transmission:	Automatic
GVWR:	7100	Test Weight:	5000	Cylinders:	8
Odometer:	5320	Certification:	California	VLT Record #:	00028
Fuel Type:	Gasoline	Exhaust:	Single	Inspection Reason:	Pre-test

Overall Test Results
PRE-TEST INSPECTION
(Not an Official Inspection)

Emission Control Systems Visual Inspection/Functional Check Results

(Visual/Functional tests are used to assist in the identification of crankcase and cold start emissions which are not measured during the ASM test)

Result	ECS	Result	ECS	Result	ECS
Pass	PCV	N/A	Thermostatic Air Cleaner	Pass	Fuel Evaporative Controls
Pass	Catalytic Converter	N/A	Air Injection	Pass	MIL/Check Engine Light
N/A	EGR Visual	Pass	Vacuum Lines to Sensors/ Switches	Pass	Carb./Fuel Injection
N/A	EGR Functional			Pass	Other Emission Related Components
Pass	Fuel Cap Functional	N/A	Ignition Timing:		
Pass	Fuel Cap Visual	Pass	Wiring to Sensors	Pass	Oxygen Sensor
Pass	Spark Controls	N/A	Fillpipe Restrictor	Pass	Liquid Fuel Leaks
N/A	Fuel Evaporative Controls Functional				

ASM Emission Test Results

		$\%CO_2$	$\%O_2$	HC (PPM)			CO (%)			NO (PPM)			
Test	RPM	MEAS	MEAS	MAX	AVE	MEAS	MAX	AVE	MEAS	MAX	AVE	MEAS	Results
15 mph	1301	15.1	0.0	101	5	0	0.51	0.01	0.00	982	29	1	PASS
25 mph	1290	15.1	0.0	90	5	0	1.00	0.01	0.00	840	25	2	PASS

MAX = Maximum Allowable Emissions AVE = Average Emissions For Passing Vehicles MEAS = Amount Measured

Smog Check Inspection Station Information

CANOGA SMOG CENTER
21412 HART ST.#A, CANOGA PARK, CA 91303
(818)887-7050
Station Number: TC249342

Technician Name/Number: VO, THEN/EA147024
Repair Tech Name/Number:
Software Version/EIS Number: 0403/ES987690

I certify, under penalty of perjury, under the laws of the State of California, that I performed the inspection in accordance with all bureau requirements, and that the information listed on this vehicle inspection report is true and accurate.

4/23/09
Date

Technician's Signature

HH2 = 99.9% EMISSION REDUCTION

Cupcake

“too lean”

“too rich”

“just right”

Other Important Combustion Reactions

Sulfur Dioxide (SO_2)

(Sulfur in Fuel) + O_2 + N_2 $\rightarrow$ SO_2 + others

Hydrogen (H_2)

$$2H_2 + O_2 \rightarrow 2H_2O + \text{heat}$$

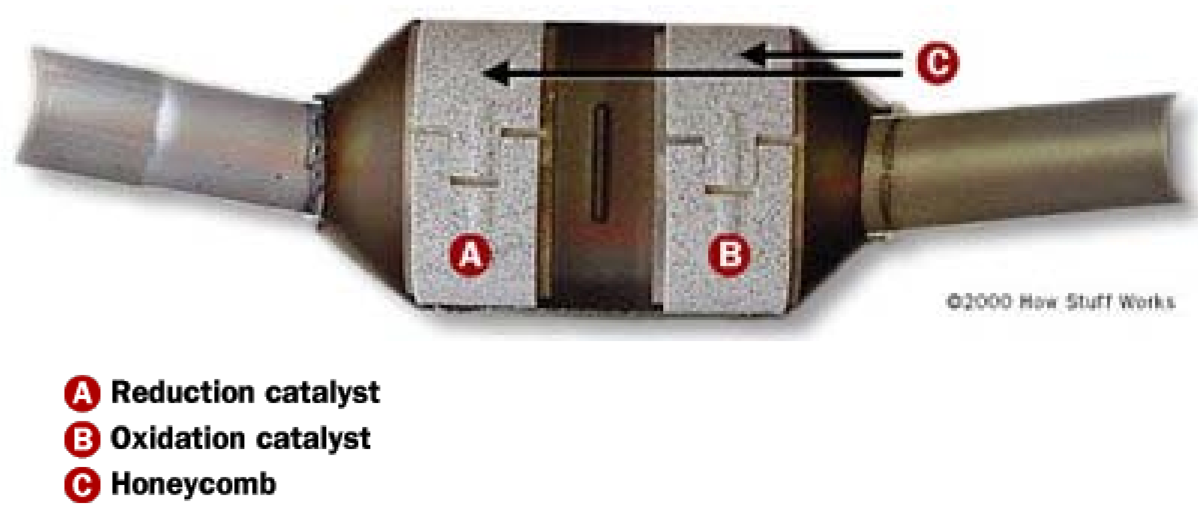
***Note**: hydrogen gas, however, must be produced by some other means, usually through hydrocarbon combustion/gasification (i.e. hydrogen is not an energy "source").*

Emission Control Technologies
(Air pollution mitigation, non-CO_2)

Some common control technologies
(“traditional air pollutants”, not CO_2)

- **Mobile Sources (Autos, other mobiles sources …)**
  - Catalytic Converters (1970s, controls CO, HCs, NOx)
  - Reformulated Gasoline (Calif., 1990s, ozone precursors … i.e. ROGs and VOCs)
- **Stationary Sources (Power plants, refineries, etc …)**
  - Sulfur Dioxide “scrubbers” (removes SO2)
  - Flares (burns excess HCs, esp. during accidents)

Catalytic Converter (Three-Way)



cross-section

Catalytic Converter (Three-Way)

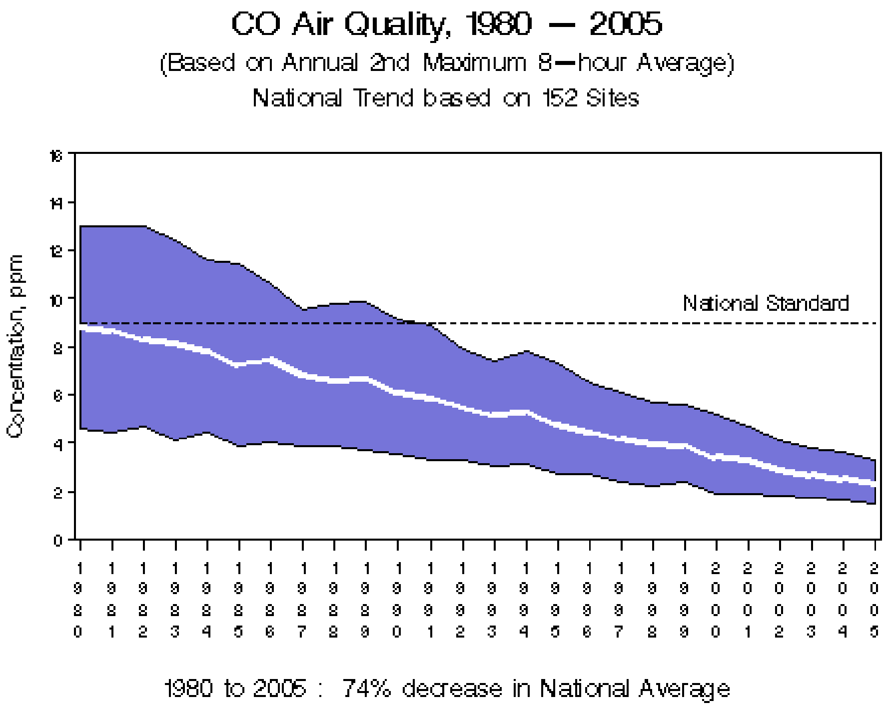
- **Made of platinum and rhodium (honeycomb)**

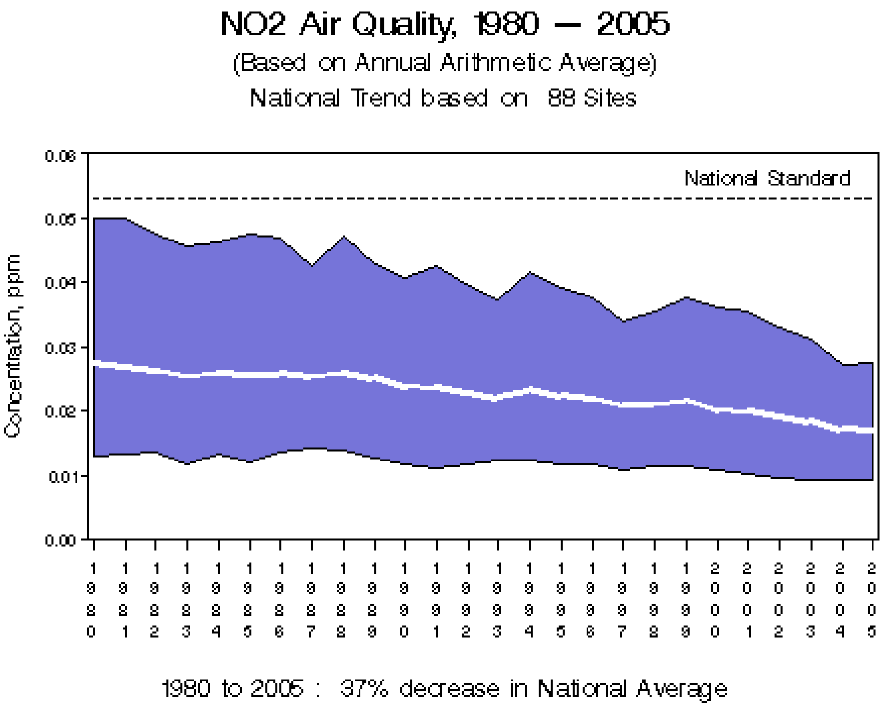
- **History**
  - Mandated by Clean Air Act in 1970
  - For post-1975 automobiles

- **NO_x Reduction**
  - $2NO \Rightarrow N_2 + O_2$ or $2NO_2 \Rightarrow N_2 + 2O_2$
  - ‘A’ on diagram on previous slide

- **CO and HC Oxydation**
  - $2CO + O_2 \Rightarrow 2CO_2$
  - Similar type reactions for HCs
  - ‘B’ on diagram on previous slide

Improvements in U.S. Air Quality …

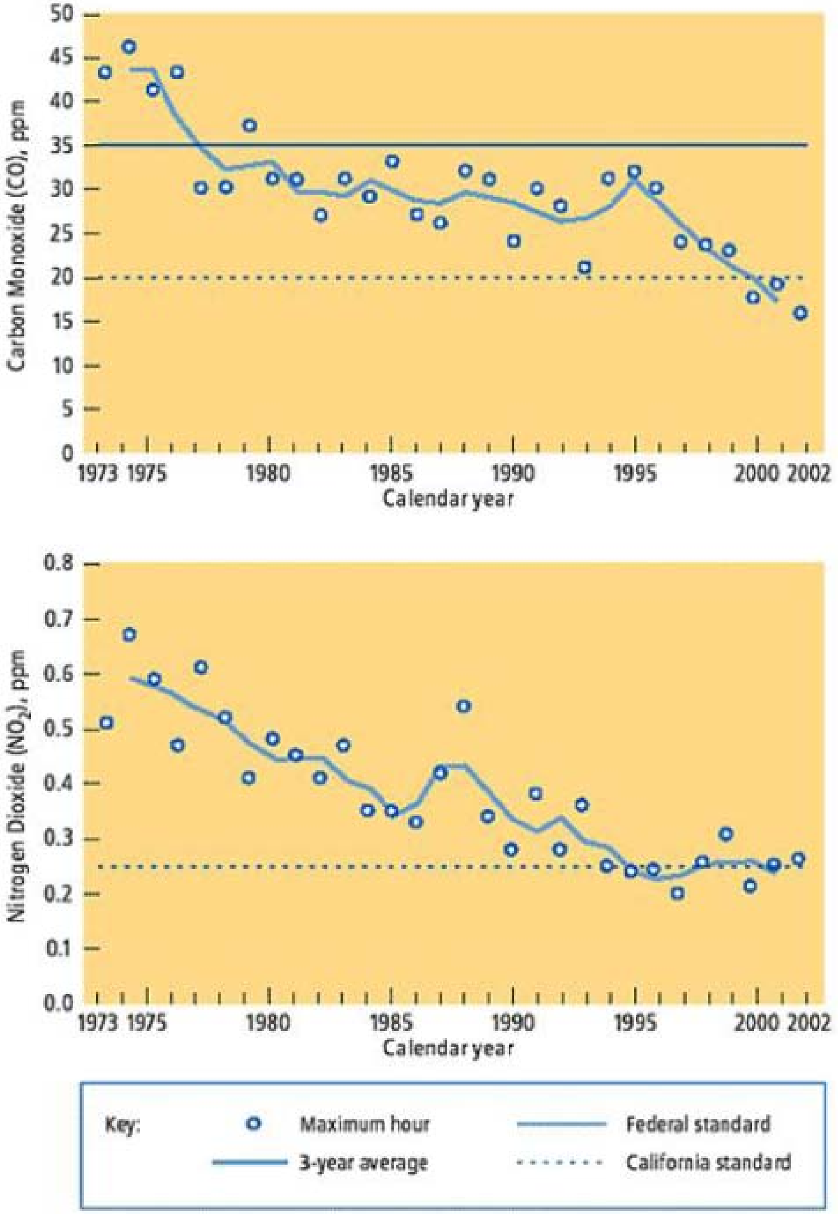




Carbon Monoxide

Nitrogen Dioxide

Improvements in California Air Quality (1) …



CARBON MONOXIDE

NITROGEN DIOXIDE

Reformulated Gasoline (RFG)

- **History**
  - Mandated by Clean Air Act in 1990 for high pollution areas (e.g. Calif.)
  - Aim to reduce ozone (O_3) and toxics (TAC) concentrations (e.g. benzene)
- **Blend alcohol additives into gasoline**
- **Results …**
  - Reduced fuel volatility (reduced evaporative HC emissions)
  - Alcohol additives less photochemically reactive (reduced ozone)
- **Common additives**
  - Ethanol
  - Methyl Tri-Butyl Ether (MTBE)

Improvements in California Air Quality (2) …

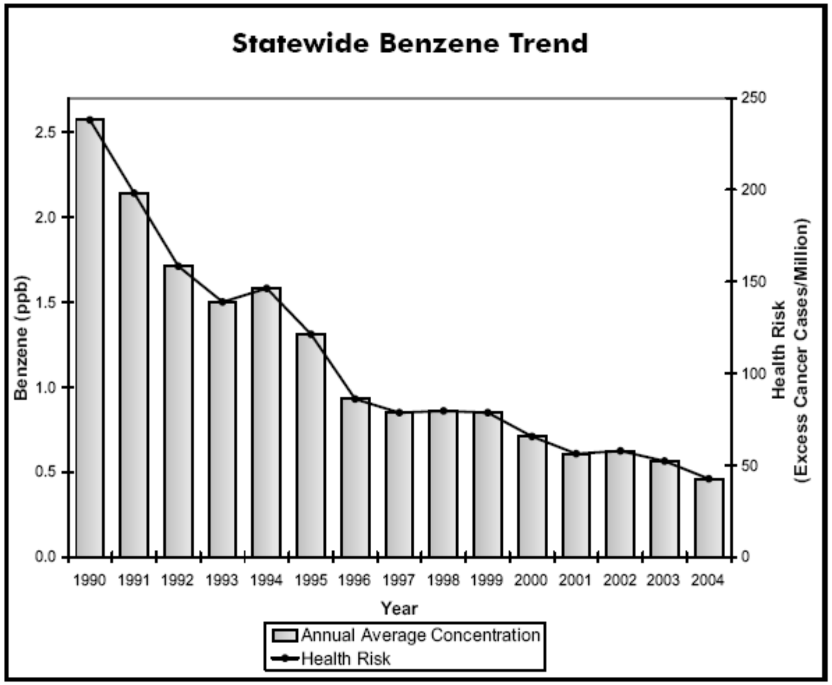


Figure 5-3

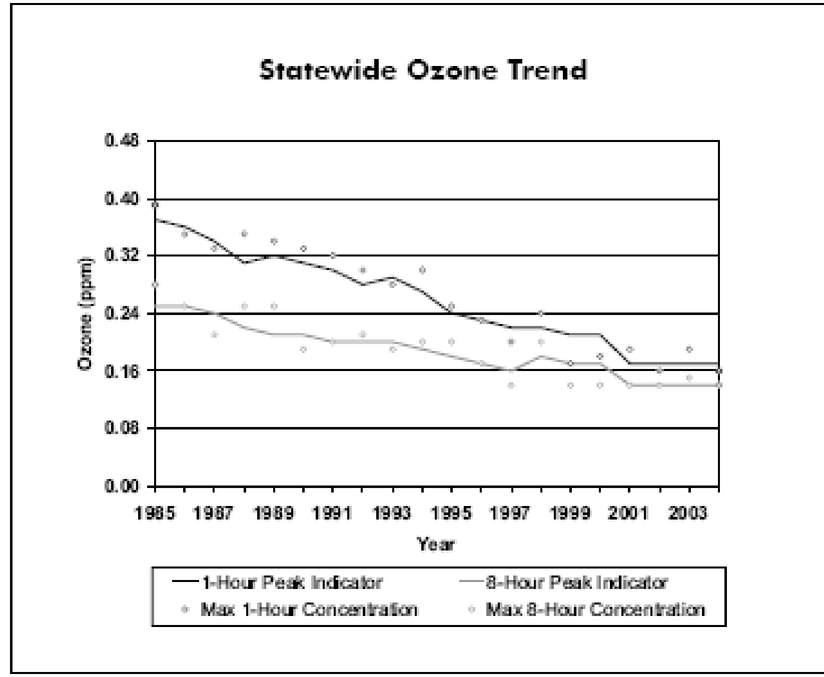
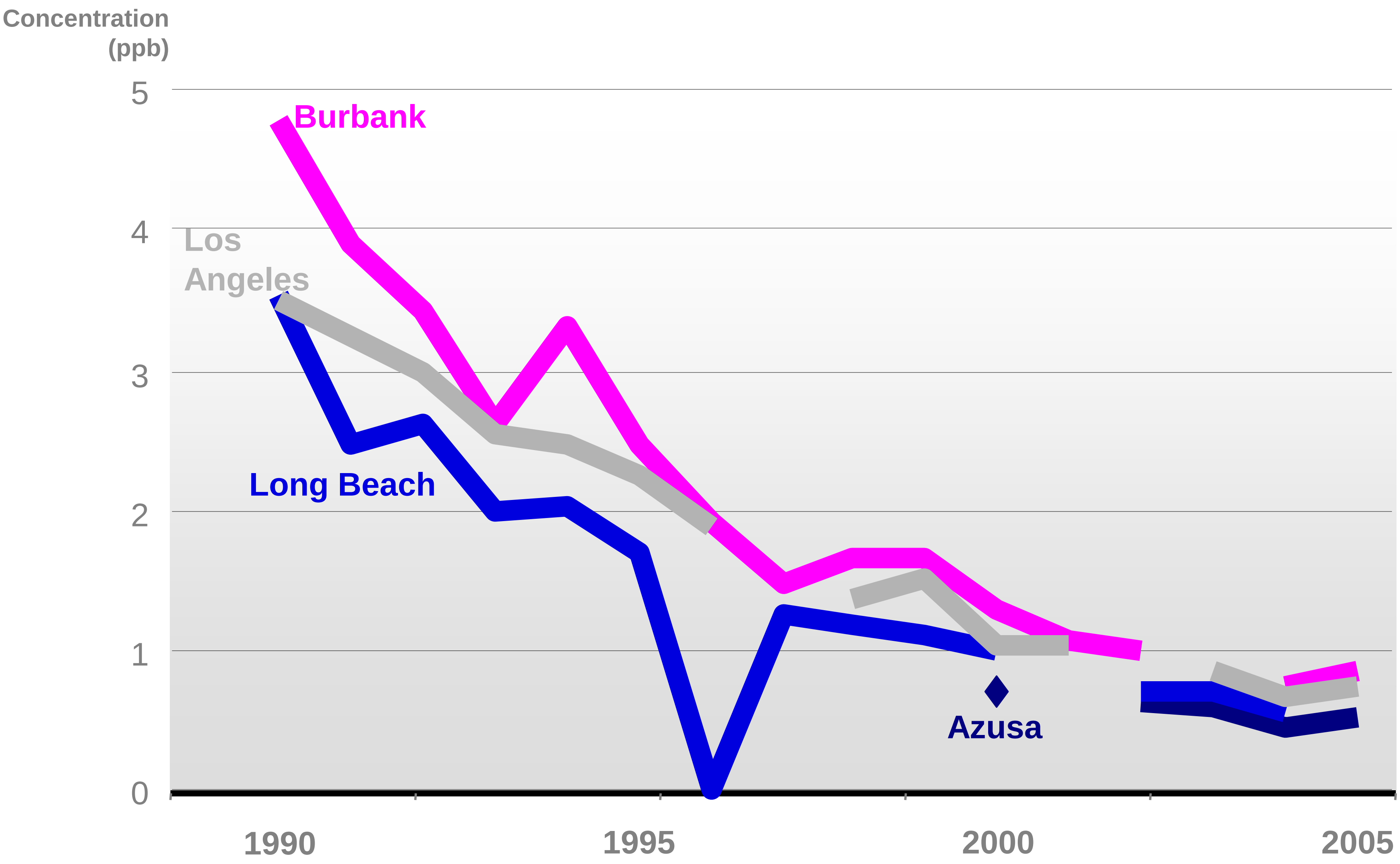


Figure 3-4

BENZENE

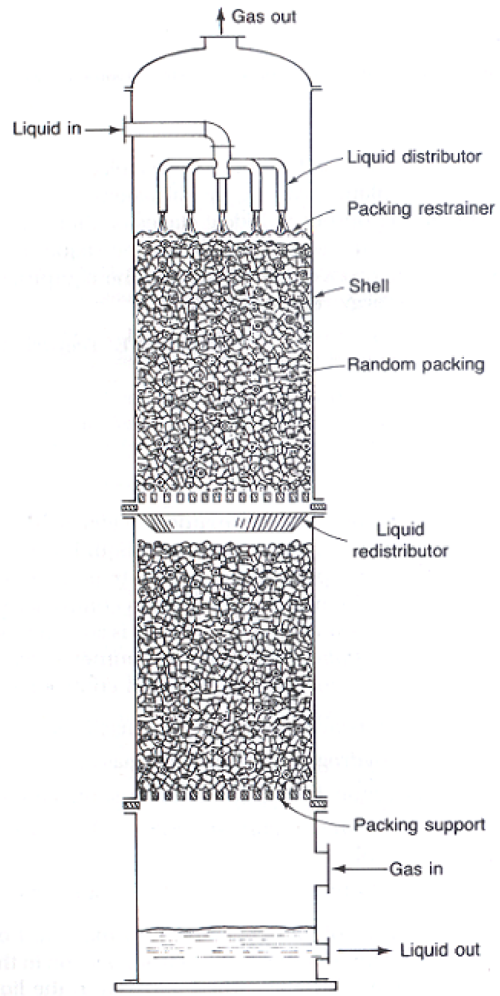
OZONE

Ambient Benzene:
CARB Air Toxics Network



Stationary Source Control Device: Absorption Scrubbers (SO_2 reduction)

Figure 13.1 Schematic diagram of a packed gas absorption tower.



Adapted from Treybal, 1968.

SO2-laden combustion gasses pas from bottom to top through wet foam packing in scrubber tower. SO2 in gas is absorbed into the water coating the foam packing. SO2-free air then passes out the top of the scrubber.

Stationary Source Control Device: Flares

Refineries and chemical plants are equipped with these to burn off waste, especially during accidents. In this case, the accidental release gasses are routed to flare to be burned off.

Alternative Energy Strategies
(CO_2 mitigation, slides to be added …)

Control Strategies for CO_2 Emissions …

- **Increase Energy Efficiency**
  - Same amount of work using less fossil fuel input energy
  - Less CO_2 emissions for same amount of work

- **Use a less CO2-emitting energy sources**
  - Hydroelectric - Nuclear - Biofuels
  - Geothermal - Solar
  - Wind - Electric, Hydrogen, Hybrid Vehicles

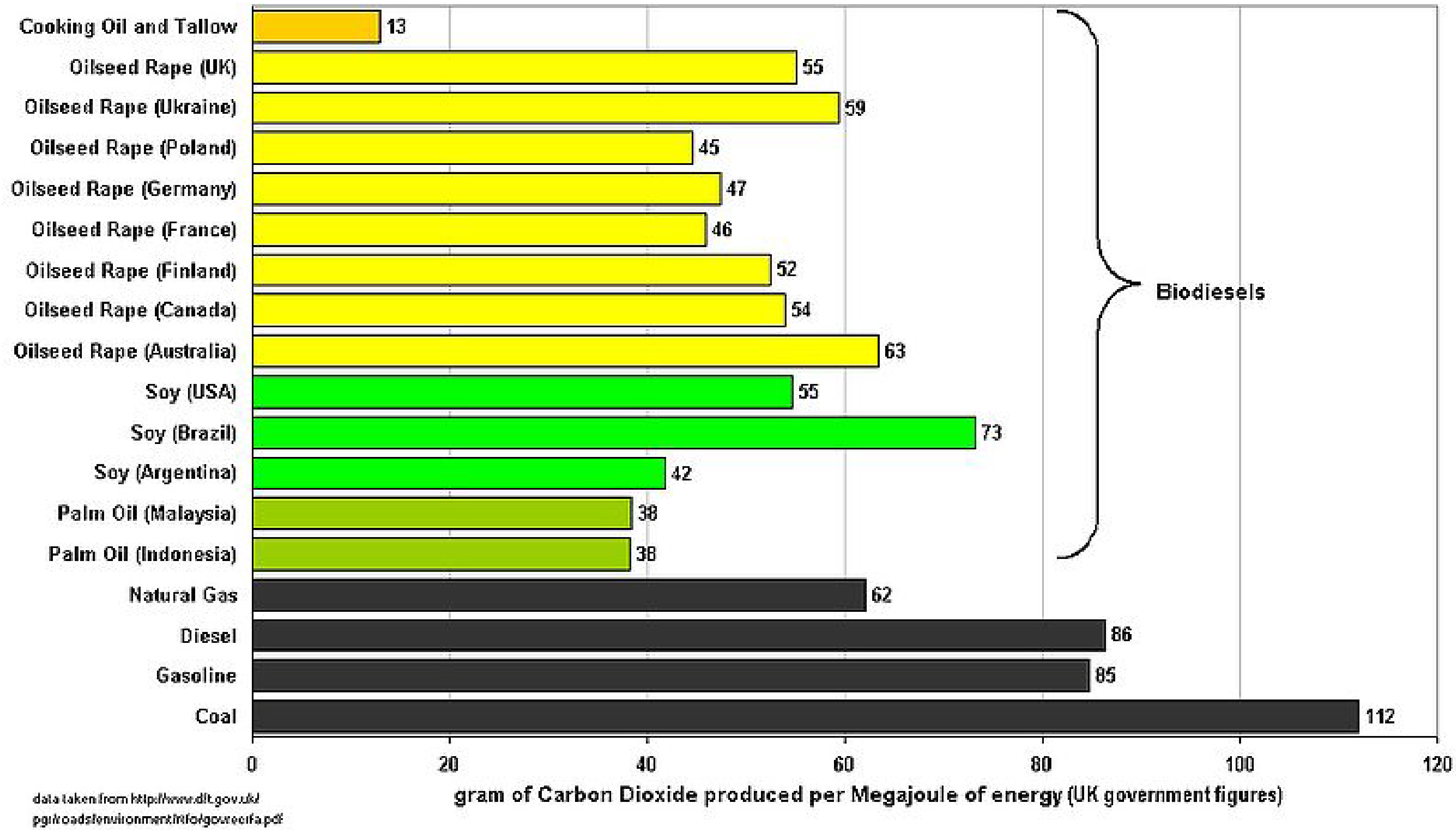
- **Carbon Sequestration (Capture and Storage)**
  - Sequestration: Carbon capture and storage underground
  - IGCC, "Future Gen" (U.S. Department of Energy program)
  - A flagship "clean coal" technology for CO_2 mitigation

- **Geo-Engineering**
  - Mirrors in space (reflect sunlight …)
  - Huge Aerosol Injection to Stratosphere (reflect sunlight …)
  - Large phytoplankon planting in oceans (absorb CO_2)
  - Large CO_2 "scrubbers" to pull CO_2 out of air
  - Etc …

Carbon Emission Intensity

- Carbon emission intensity is how much CO2 (or CO2-eq) is emitted per amount of energy obtained in burning fuel
- Expressed, for example, as
  - Grams CO2 per Mjoule energy obtained
  - Tons CO2 per BTU obtained (british units)
  - Others …
- CO2 emitted comes from both <u>direct</u> and <u>indirect</u> emissions. Carbon intensity therefore accounts for CO2 emitted during the <u>entire process</u> of production of fuel through burning of fuel ("well-to-wheel").

Carbon emission intensity of various carbon-based fuels …



"Graph of UK figures for the carbon intensity of biodiesels and fossil fuels. This graph assumes that all biodiesels are burnt in their country of origin. It also assumes that the diesel is produced from pre-existing croplands rather than by changing land use"

http://en.wikipedia.org/wiki/Emission_intensity

An illustration of indirect carbon emissions … standard industrial production of hydrogen gas.

Using natural gas (methane, CH_4) to produce hydrogen (H_2) …

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$H_2O + CO \rightarrow CO_2 + H_2$$

CO2 emissions,
i.e. "indirect" emissions.
unless somehow
captured somehow …

Hydrogen fuel
for transportation
(via pipeline, fuel cells, ?).
No direct CO2 emissions
when "burning" hydrogen.
See slide 14 …

Emission Intensity of other air pollutants

(CO2 and others …)

Fossil Fuel Emission Levels
- Pounds per Billion Btu of Energy Input

Pollutant	Natural Gas	Oil	Coal
Carbon Dioxide	117,000	164,000	208,000
Carbon Monoxide	40	33	208
Nitrogen Oxides	92	448	457
Sulfur Dioxide	1	1,122	2,591
Particulates	7	84	2,744
Mercury	0.000	0.007	0.016

Source: EIA - Natural Gas Issues and Trends 1998

→

cleaner to dirtier

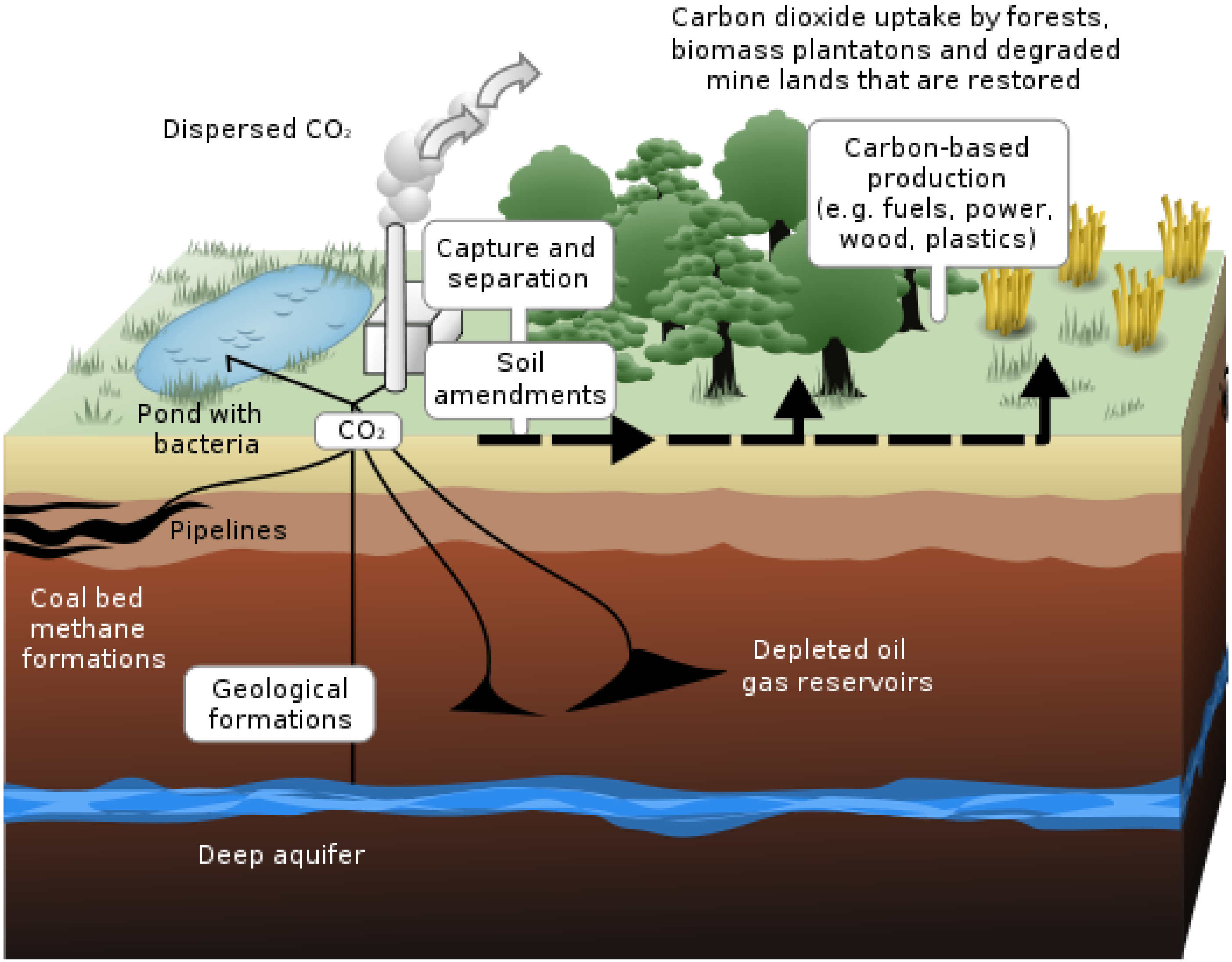
Gasification & Carbon Capture and Storage (CCS)

- Gasify fossil fuel to produce …
  - Hydrogen gas (H_2)
  - Carbon Dioxide (CO_2)
- Burn H_2 for energy
  - Steam or gas turbine for electricity
  - Fuel cell for transportation vehicle
- Capture and then store CO_2 underground
  - Oil & Gas Reservoirs
  - Coal Seams
  - Ocean

http://www.fossil.energy.gov/programs/powersystems/futuregen/

Hyperlink …

→ Carbon Capture and Storage (CCS)



Another consideration …“peak oil”

What will be our electricity source?
Conventional crude oil production to decline in future years
(Similar story with natural gas, although not as imminent as with oil)

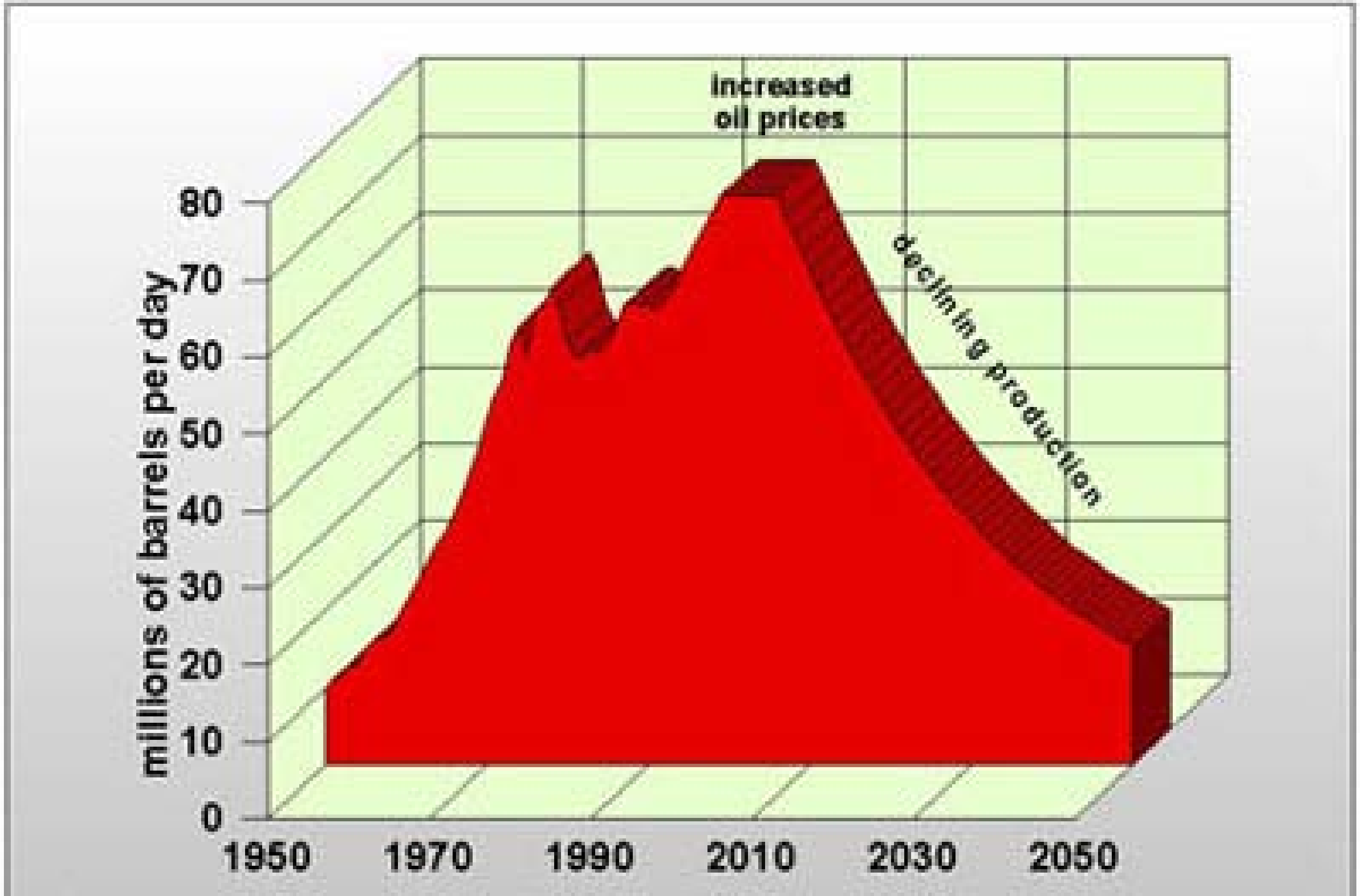
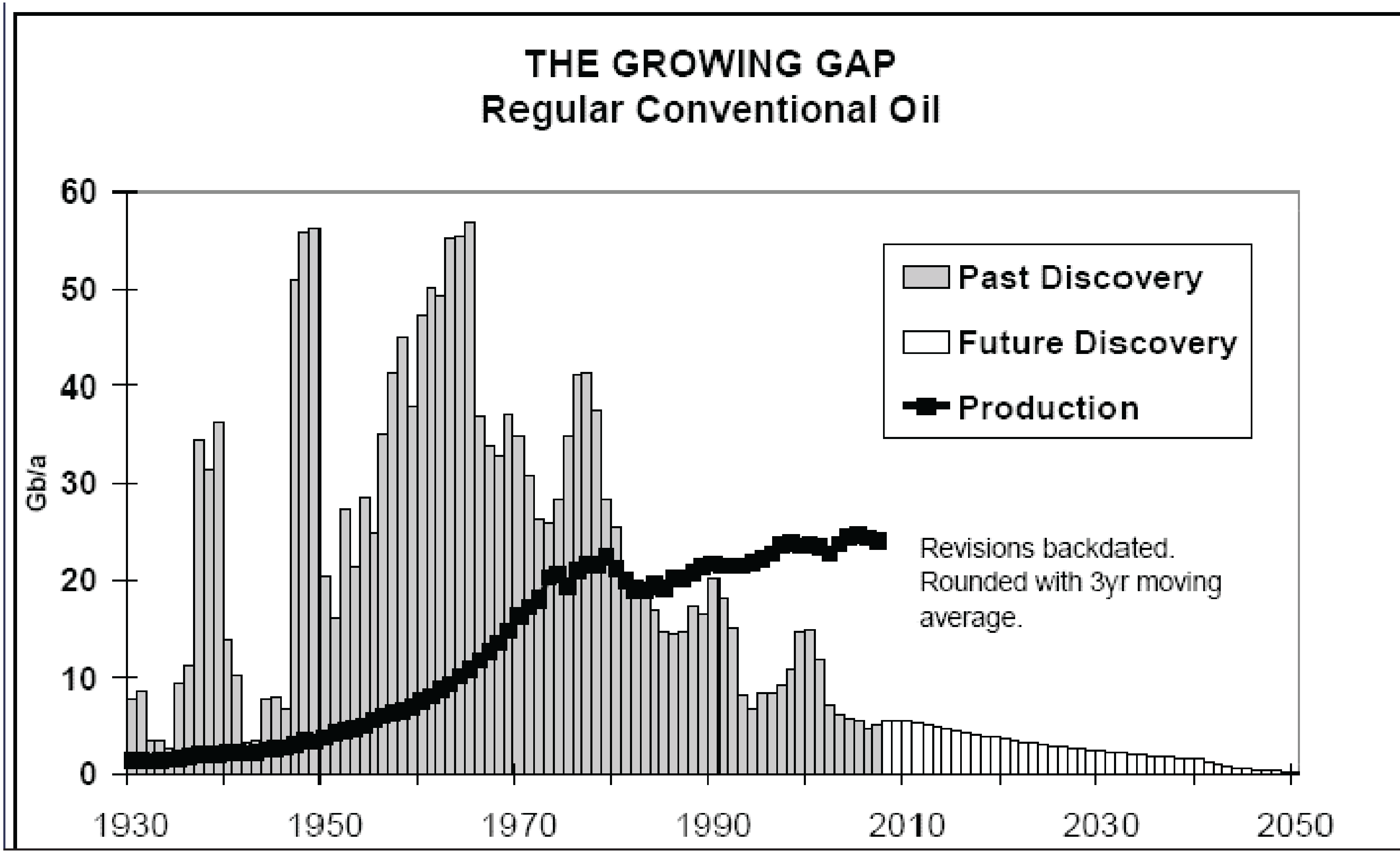


Figure 2. Actual and Projected Worldwide Oil Production



THE GROWING GAP
Regular Conventional Oil
60
50
40
30
20
10
0
Gb/a
1930
1950
1970
1990
2010
2030
2050
Past Discovery
Future Discovery
Production
Revisions backdated.
Rounded with 3yr moving
average.

What other energy resources could replace oil & natural gas?

How about coal?

Fossil Fuel Emission Levels
- Pounds per Billion Btu of Energy Input

Pollutant	Natural Gas	Oil	Coal
Carbon Dioxide	117,000	164,000	208,000
Carbon Monoxide	40	33	208
Nitrogen Oxides	92	448	457
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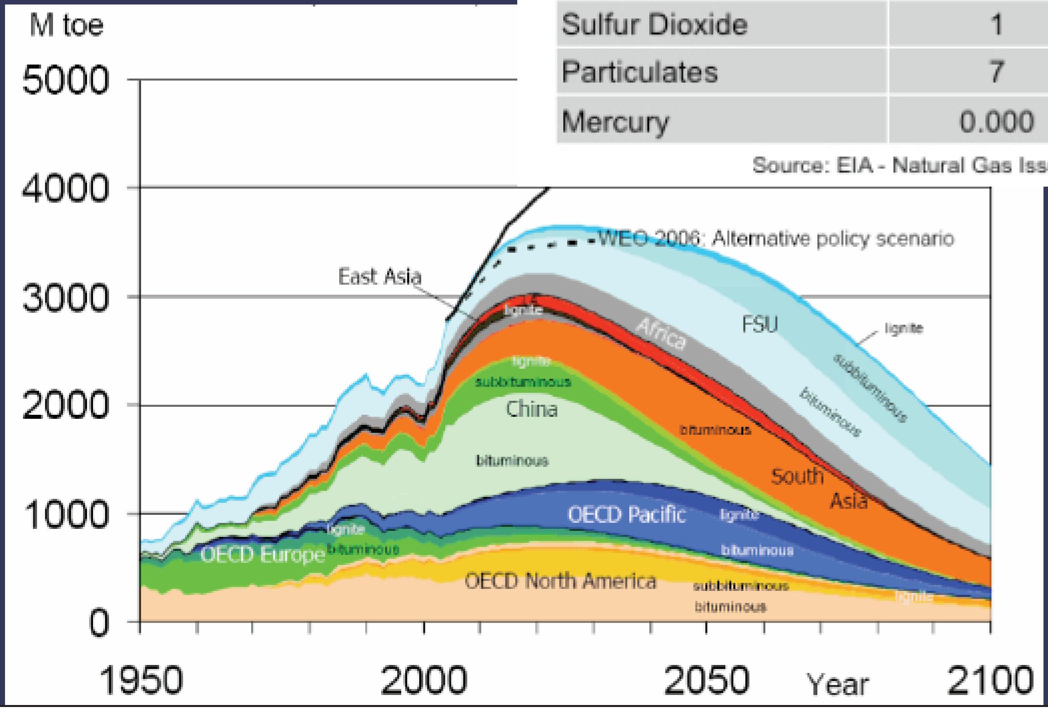
Particulates	7	84	2,744
Mercury	0.000	0.007	0.016

Source: EIA - Natural Gas Issues and Trends 1998



Peak Coal within 20 years?

“Unconventional” Oil …

Non Fossil Energy Sources: Electricity …

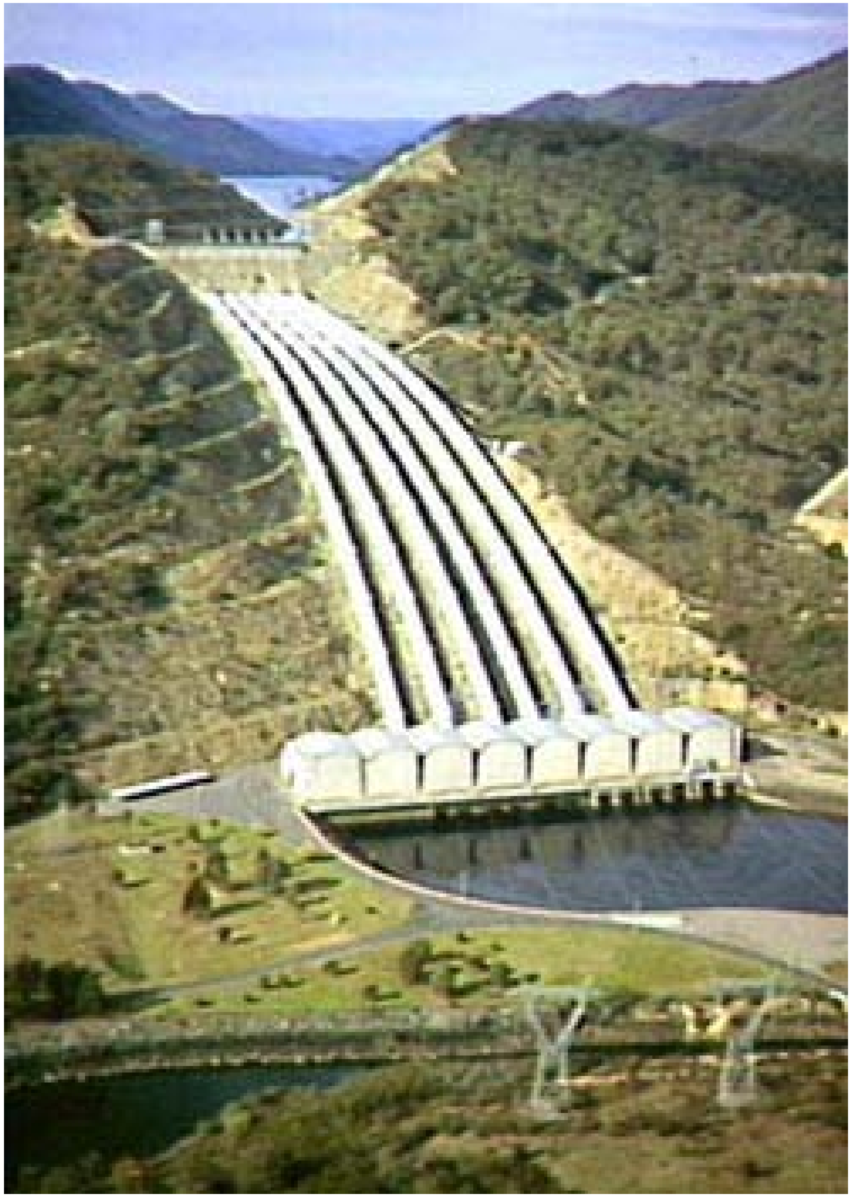
Solar …

Wind …

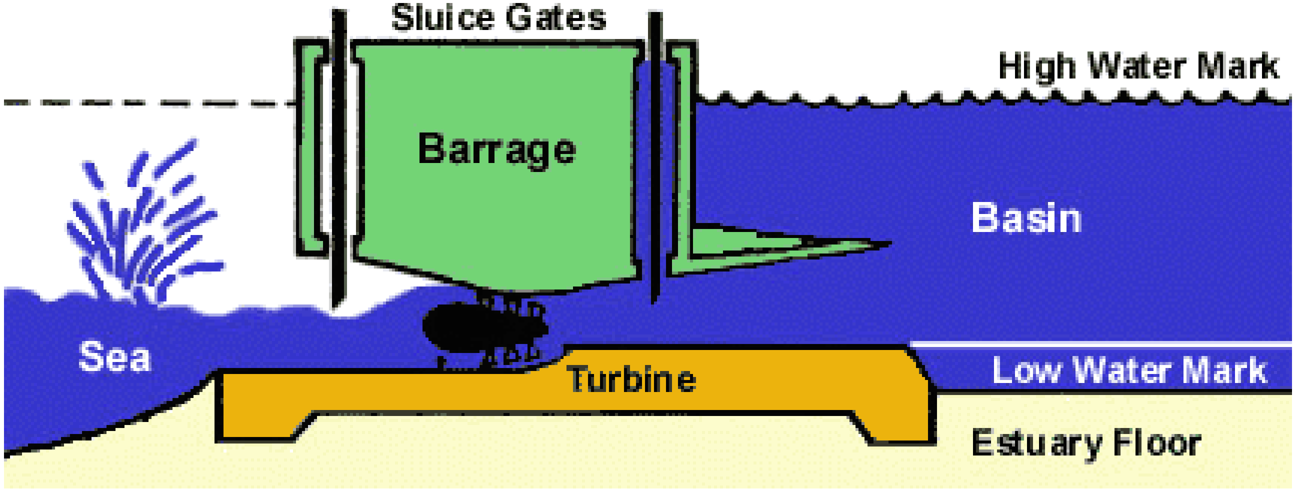
Altamont Pass, California

Geothermal

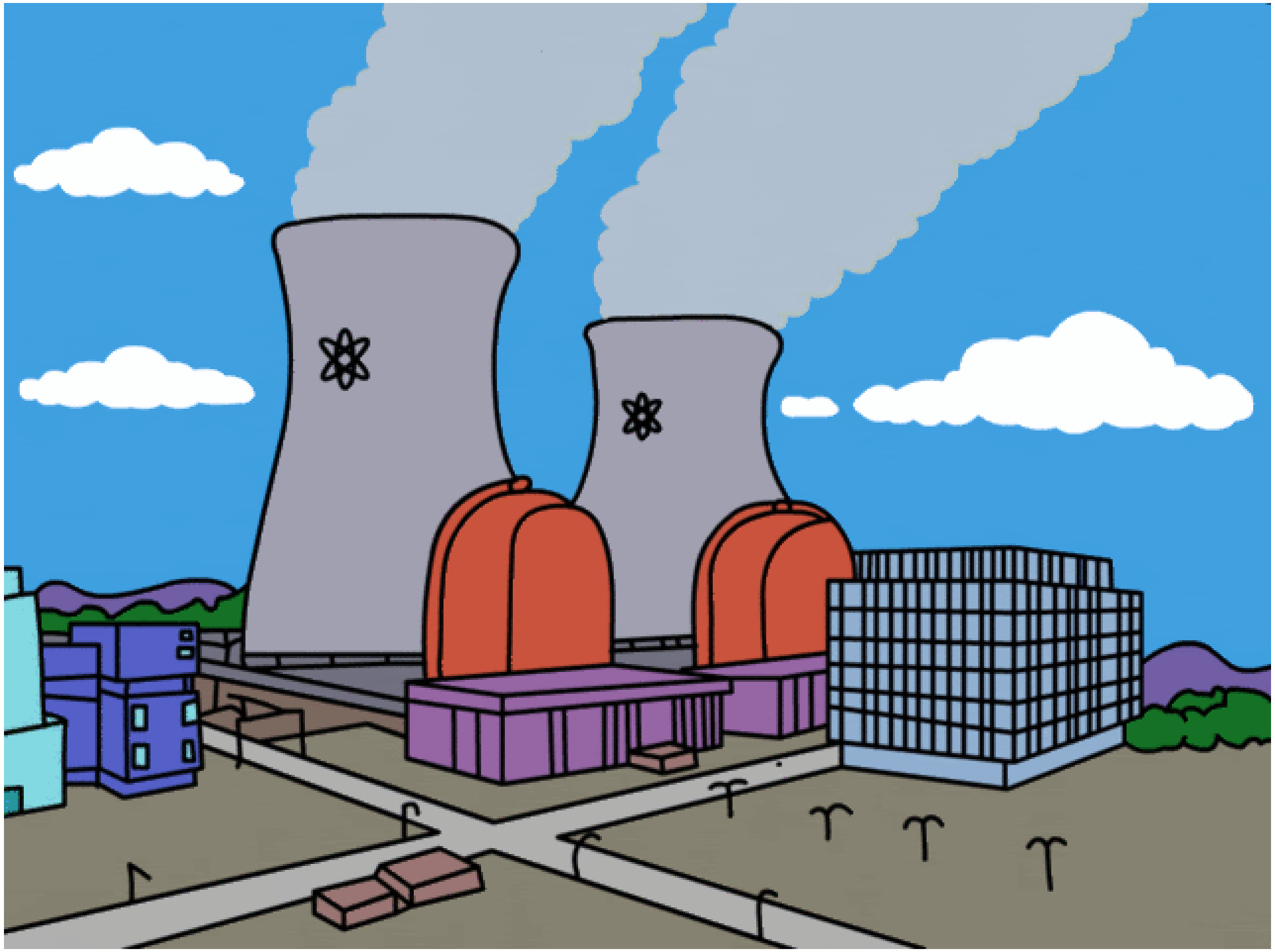
Hydro power



Tidal Power


Sluice Gates
High Water Mark
Barrage
Basin
Sea
Turbine
Low Water Mark
Estuary Floor

Nuclear



“Alternative” Transportation Fuels:

Ethanol

- Corn Based (U.S.)
- Sugar Cane (Brazil)
- Switch Grass (future?)
- Falling out of favor:
  - May not actually be “carbon neutral”
  - Takes more energy to produce than it gives off when burned
  - Drives up cost of food
- Ethanol still used as additive to mitigate air pollution

(see previous slides regarding Reformulated Gasoline in early part of lecture)

Biodiesel

- Soybeans
- Similar problems as ethanol (may not be as bad though)
- Grease (a waste product, waste to energy, ☺)

Some Multiple Exam Questions (Exam #4)

The catalytic converter on modern automobiles is designed to control emissions of the following species emitted from automobiles:

a) Carbon monoxide (CO) and ozone (O_3)
b) Carbon monoxide (CO) and nitrogen oxides (NO_x)
c) Carbon dioxide (CO_2) and ozone (O_3)
d) Carbon dioxide (CO_2) and nitrogen oxides (NO_x)

A coal combustion plant is constructed. The plant will contain numerous ‘flares’ and a ‘scrubber’. Based on this, what can be accurately said about pollution control at the plant?

a) All three of the following emissions are controlled: Carbon Dioxide, Sulfur Dioxide, and accidental emissions.
b) Carbon Dioxide and accidental emissions are controlled, but not Sulfur Dioxide
c) Sulfur Dioxide and accidental emissions are controlled, but not Carbon Dioxide
d) Sulfur Dioxide and Carbon Dioxide are controlled, but not accidental emissions.

Which of the following best characterizes the sequence of steps in forming high ozone concentrations in urban areas?

a) High O_3 emissions in the morning, followed by high rates of chemical production of O_3 in the late morning and afternoon due to rising temperatures during the day.
b) High O_3 emissions in the morning, followed by low rates of chemical destruction of O_3 in the late morning and afternoon due to rising temperatures during the day.
c) High NO and ROG emissions in the early morning, followed by high chemical formation of NO_2 and O_3 in the late morning and afternoon.
d) High NO and CO emissions in the early morning, followed by high chemical formation of CO_2 and O_3 in the late morning and afternoon.

Carbon Intensity of Unconventional vs. Conventional Oil …

See links below … does unconventional oil release more CO2 Than conventional oil? How much more (in terms of emission intensity)? Why … i.e. what is it about unconventional oil that makes it “dirtier” with respect to CO2 emissions?

Be prepared to answer multiple choice and/or short answer question on Exam #4 on this topic.

http://www.wri.org/publication/content/10339
http://en.wikipedia.org/wiki/Oil_sands