Air Pollution
ENV-409

Emissions and Control

Why learn about emissions

- Which sources are responsible for pollutant emissions?
- Forms the basis of our ability to
  - evaluate pollution interventions
  - forecast future air quality and climate scenarios in response to changes in mitigation strategies, technological innovation, or human activity

Topics

Primary pollutants

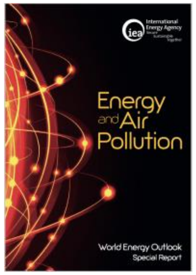
- SO_2
  - burning sulfur or material containing sulfur
- NO_x
  - burning fuel in air (which contains molecular nitrogen)
- CO
  - incomplete combustion of carbonaceous fuel
- Particulate matter (aerosols)
  - natural and anthropogenic sources

Precursors for secondary pollutants (O_3 and PM)

  - VOCs (hydrocarbons)
  - NH_3

Greenhouse gases

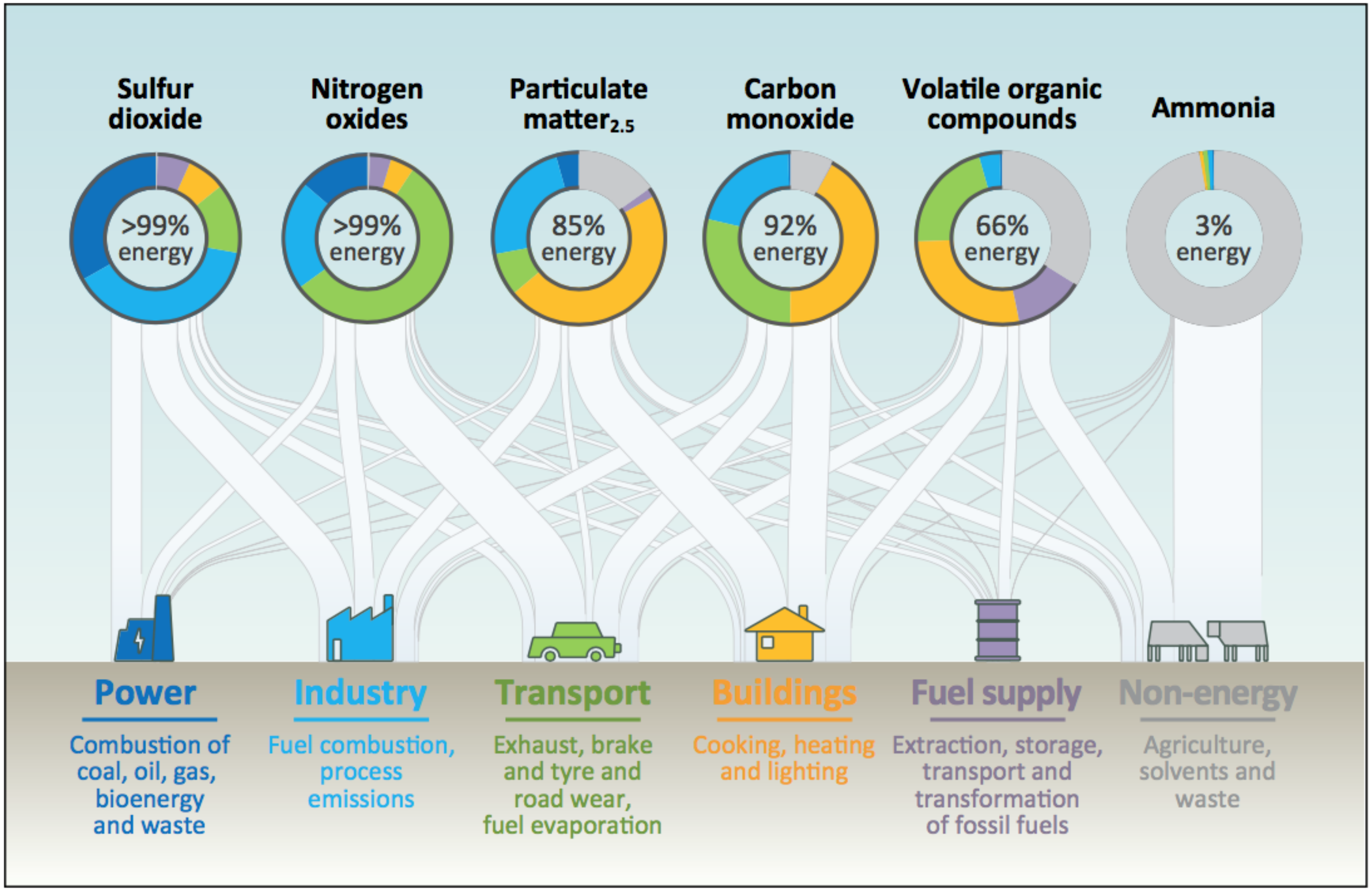
- CO_2 (not primary pollutant)
  - product of complete combustion
  - many sources (and natural sinks)



Energy and Air Pollution

World Energy Outlook Special Report

Figure 1.3 ▷ Selected primary air pollutants and their sources, 2015



Framework

The emission (rate) E is often calculated as an emission factor (emission rate per unit) e multiplied by its activity (number of units) A for substance i and source class s at position $\mathbf{r}$ and time t:

$$E_{i,s}(\mathbf{r},t) = e_{i,s} \times A_s(\mathbf{r},t)$$

- Sources (source class):
  - Fossil fuel combustion
  - Biogenic emissions
  - Natural: dust, sea spray, volcanic
  - Agricultural
- Emission environment/conditions
- Chemical mechanisms
- Methods for estimating emissions

Examples of possible units for activity (A):

- vehicle
- vehicle km traveled
- kg of fuel
- hectacre
- powerplant

(We will consider this equation as a framework, but will discuss emissions qualitatively.)

MECHANISMS

Combustion

High temperature (often in excess of 2000 K) allows

- rapid oxidation of hydrocarbons and carbon monoxide to carbon dioxide and water, but
- also makes it possible to form nitric oxide (NO) from oxidation of molecular nitrogen (N_2)

Fuel + Oxidant → Combustion products

Carbon monoxide, carbon dioxide, and hydrocarbons from combustion

Produced from complete and incomplete combustion

Stoichiometric equation for complete combustion of a hydrocarbon molecule in pure oxygen:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$$

Examples:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ methane

$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$ octane

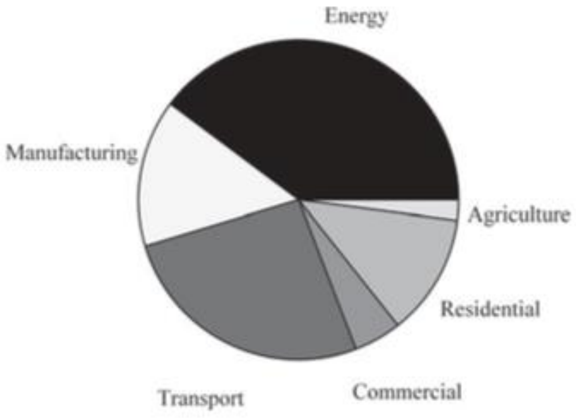


Fig. 1.1 EU27 CO_2 emissions by sector and mode of transport in 2009 adapted from European Commission (2012a)

Battin-Leclerc et al., 2013

The stoichiometric condition is a logical reference point for comparison of systems operating on different fuels.

Combustion of a hydrocarbon in air:

$$\mathrm{C_xH_y} + \left(x + \frac{y}{4}\right)(\mathrm{O_2} + \frac{79}{21}\mathrm{N_2}) \rightarrow x\mathrm{CO_2} + \frac{y}{2}\mathrm{H_2O} + \left(x + \frac{y}{4}\right)\frac{79}{21}\mathrm{N_2}$$

For every mole of fuel burned, $(1 + 79/21)(x + y/4)$ of air are required. The molar fuel/air ratio for stoichiometric combustion is $1/[(1 + 79/21)(x + y/4)]$. $(1 + 79/21)(x + y/4) + y/4$ moles of combustion products are generated; the product mole fractions for complete combustion of this hydrocarbon fuel are

$$\begin{aligned} y_{\mathrm{CO_2}} &= \frac{x}{(1+79/21)(x+y/4)+y/4} \\ y_{\mathrm{H_2O}} &= \frac{y/2}{(1+79/21)(x+y/4)+y/4} \\ y_{\mathrm{N_2}} &= \frac{(79/21)(x+y/4)}{(1+79/21)(x+y/4)+y/4} \end{aligned}$$

The fuel/air ratio is is used to define operating conditions of a combustor; there are several normalized metrics used to characterize this quantity. One common metric is the equivalence ratio, which defines the fuel/air ratio noramlized with respect to the stoiciometric fuel/air ratio (m denotes mass and n denotes number of moles):

$$\phi = \frac{(m_f/m_a)_{\text{actual}}}{(m_f/m_a)_{\text{stoich}}} = \frac{(n_f/n_a)_{\text{actual}}}{(n_f/n_a)_{\text{stoich}}}$$

Many combustion systems are operated with an excess of air ($\phi < 1$; "fuel-lean" conditions) to ensure complete combustion of the fuel.

$$\mathrm{C_xH_y} + \frac{1}{\phi}\left(x + \frac{y}{4}\right)(\mathrm{O_2} + \frac{79}{21}\mathrm{N_2}) \to x\mathrm{CO_2} + \frac{y}{2}\mathrm{H_2O} + \left(\frac{1}{\phi} - 1\right)\left(x + \frac{y}{4}\right)\mathrm{O_2} + \frac{1}{\phi}\left(x + \frac{y}{4}\right)\frac{79}{21}\mathrm{N_2}$$

For every mole of fuel burned, $(1/\phi)(1 + 79/21)(x + y/4)$ of air are required. The molar fuel/air ratio for stoichiometric combustion is $1/[(1/\phi)(1 + 79/21)(x + y/4)]$. $(1/\phi)(1 + 79/21)(x + y/4) + y/4$ moles of combustion products are generated; the product mole fractions (including oxygen) for complete combustion of this hydrocarbon fuel are

$$\begin{aligned}
y_{\mathrm{CO_2}} &= \frac{x}{(1/\phi)(1 + 79/21)(x + y/4) + y/4} \\
y_{\mathrm{H_2O}} &= \frac{y/2}{(1/\phi)(1 + 79/21)(x + y/4) + y/4} \\
y_{\mathrm{N_2}} &= \frac{(1/\phi)(79/21)(x + y/4)}{(1/\phi)(1 + 79/21)(x + y/4) + y/4} \\
y_{\mathrm{O_2}} &= \frac{(1/\phi) - 1}{(1/\phi)(1 + 79/21)(x + y/4) + y/4}
\end{aligned}$$

The composition of products in fuel-lean combustion can be approximated by element balances. Under "fuel-rich" conditions ($\phi > 1$), unburnt hydrocarbons remain in the products, and additional thermodynamic or kinetic constraints determine exhaust composition.

Example calculation of product composition (mole fractions) for CH_4 and C_8H_{18}; equivalence ratios of $\phi = 1$ and $\phi = 0.85$:

Compound	ϕ	y_{CO_2}	y_{H_2O}	y_{N_2}	y_{O_2}
CH_4	1.00	0.10	0.19	0.72	0.00
CH_4	0.85	0.08	0.16	0.73	0.03
C_8H_{18}	1.00	0.12	0.14	0.73	0.00
C_8H_{18}	0.85	0.11	0.12	0.74	0.03

Shown on right:

Concentration of CO_2, CO, O_2, and H_2O as a function of relative air/fuel ratio (also called the stoichiometric ratio). Note that it is the reciprocal of the equivalence ratio: λ = 1/ϕ. Contour lines indicate H/C molar ratio.

Wark et al., 1998

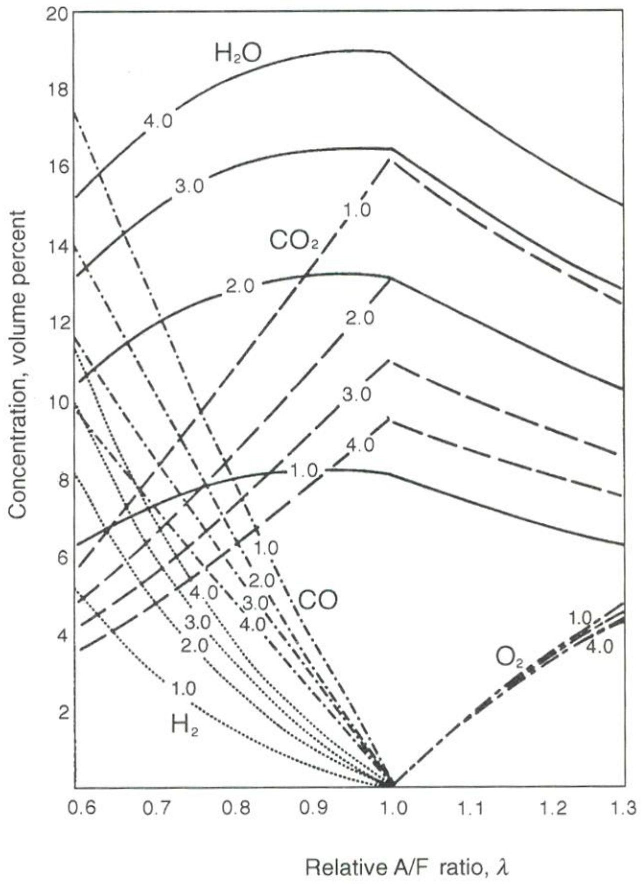
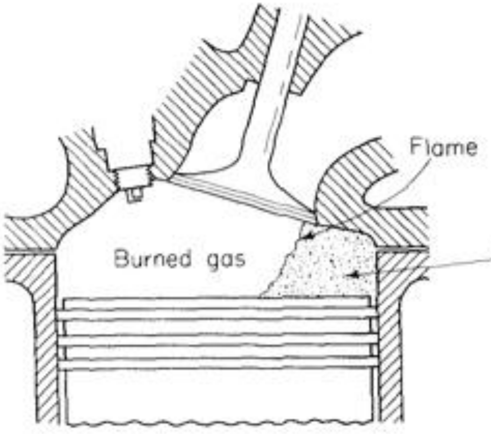


FIGURE 6-20 Relationship between concentration of combustion products of hydrocarbon fuels and relative A/F ratio. (Source: *Combustion: The Formation and Emission of Trace Species*, J. B. Edwards, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.)

Reasons for incomplete combustion

- Low temperatures
  - quenching by cylinder walls
- Insufficient oxidant
  - incomplete mixing of fuel and air (emergence of fuel-rich regions)
- Operating parameters (engine load)
- Poor equipment maintenance



Flagan and Seinfeld (1988)

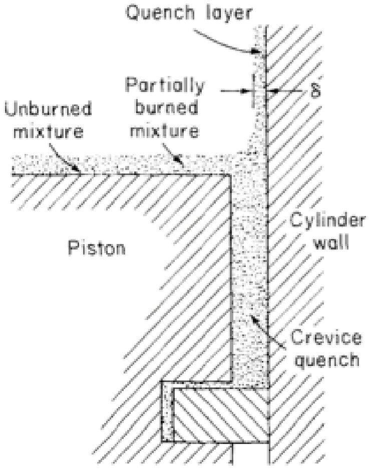


Figure 4.8 Schematic showing the quench layer and crevice volume where heat transfer to the walls may quench the combustion (Tabaczynski et al., 1972; © SAE, Inc.).

CO, CO2

Simplest "global model" (model which ignores detailed steps—i.e., individual elementary reactions—but captures the overall process converting products to reactants) for oxidation of a hydrocarbon:

$$C_xH_y + \left(\frac{x}{2} + \frac{y}{4}\right) O_2 \xrightarrow{k_1'} x\mathrm{CO} + \left(\frac{y}{2}\right) H_2O$$

$$x\mathrm{CO} + \left(\frac{x}{2}\right) O_2 \xrightarrow{k_2'} \mathrm{CO}_2$$

Kinetic expressions:

$$\begin{aligned} r_{C_xH_y} &= -k_1'[C_xH_y][O_2] \\ r_{\mathrm{CO}} &= xk_1'[C_xH_y][O_2] - k_2'[\mathrm{CO}][O_2] \\ r_{\mathrm{CO}_2} &= k_2'[\mathrm{CO}][O_2] \end{aligned}$$

Note that in the presence of excess oxygen, we can write $k_1 = k_1'[O_2]$ and $k_2 = k_2'[O_2]$ and consider this system as a first-order reaction series:

$$\overset{A}{C_xH_y} \xrightarrow{k_1} \overset{R}{\mathrm{CO}} \xrightarrow{k_2} \overset{S}{\mathrm{CO}_2}$$

Cooper and Alley, 2011

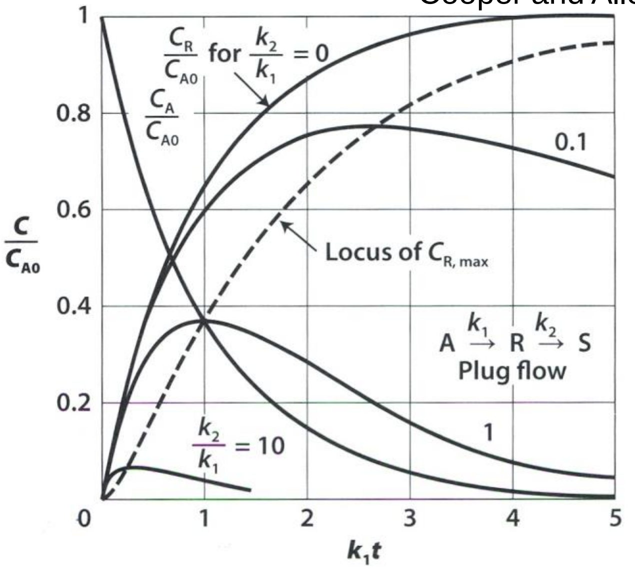


Figure 11.3
Concentration/residence time curves in a plug flow reactor for a 1:1:1 series reaction.
Note: CA, CR = concentration of A or R, respectively, mol/L
(Adapted from Levenspiel, 1962.)

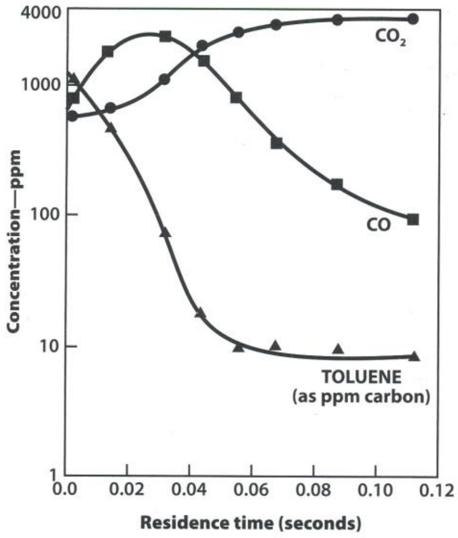


Figure 11.4
Concentration/residence time curves in a plug flow reactor for toluene, CO, and CO_2 at 1525 °F.
(Adapted from Hemsath and Susey, 1974.)

- For fuel-lean combustion (excess air present) with product temperatures below 1250 K, complete reaction of fuel with primary products CO_2, H_2O, O_2, and N_2 is a reasonable assumption.
- At higher temperatures, species that are stable at ambient temperatures can dissociate by reactions such as

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$$
$$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$$

  so that CO, H_2, and other reduced species may be present even though sufficient oxygen is available for complete combustion.
- We will approximate composition at high temperatures using principles of chemical equilibrium, which provide insight into pollutant information.

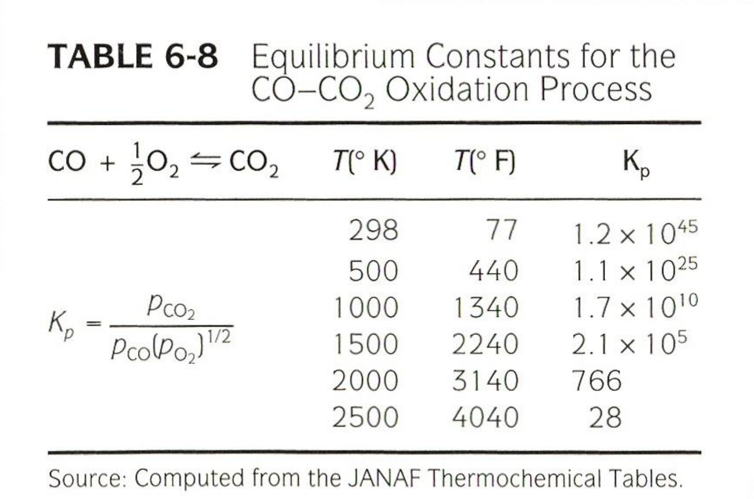


TABLE 6-8 Equilibrium Constants for the CO–CO_2 Oxidation Process

$CO + \frac{1}{2}O_2 \leftrightharpoons CO_2$	T(° K)	T(° F)	K_p
$K_p = \dfrac{p_{CO_2}}{p_{CO}(p_{O_2})^{1/2}}$	298	77	1.2×10^{45}
	500	440	1.1×10^{25}
	1000	1340	1.7×10^{10}
	1500	2240	2.1×10^{5}
	2000	3140	766
	2500	4040	28

Source: Computed from the JANAF Thermochemical Tables.

Wark et al., 1998

Example 6-8 from Wark et al., 1998

Estimate the number of moles of carbon monoxide at equilibrium in an ideal gas mixture at 2000 K if the initial mixture composition is 1.00 mole of CO, 0.55 mole of O_2, and 2.05 moles of inert N_2 at 1 atm.

$$K_p\big|_{2000\,\mathrm{K}} = 766 = \frac{p_{CO_2}}{p_{CO}(p_{O_2})^{1/2}}$$

Note that partial pressure $p_i = (n_i/n)p$ where n and p are the total moles and pressure, respectively.

$$K_p = \frac{n_{CO_2}}{n_{CO}(n_{O_2})^{1/2}}\left(\frac{p}{n}\right)^{-1/2}$$

Conservation/mole balance equations:

$$n_{CO} + n_{CO_2} = n_{CO,\mathrm{init}} = 1.00$$

$$n_{CO} + 2n_{CO_2} + 2n_{O_2} = n_{CO,\mathrm{init}} + n_{O,\mathrm{init}} = 2.10$$

$$n = n_{CO} + n_{CO_2} + n_{O_2} + n_{N_2}$$

Putting in values into equilibrium expression:

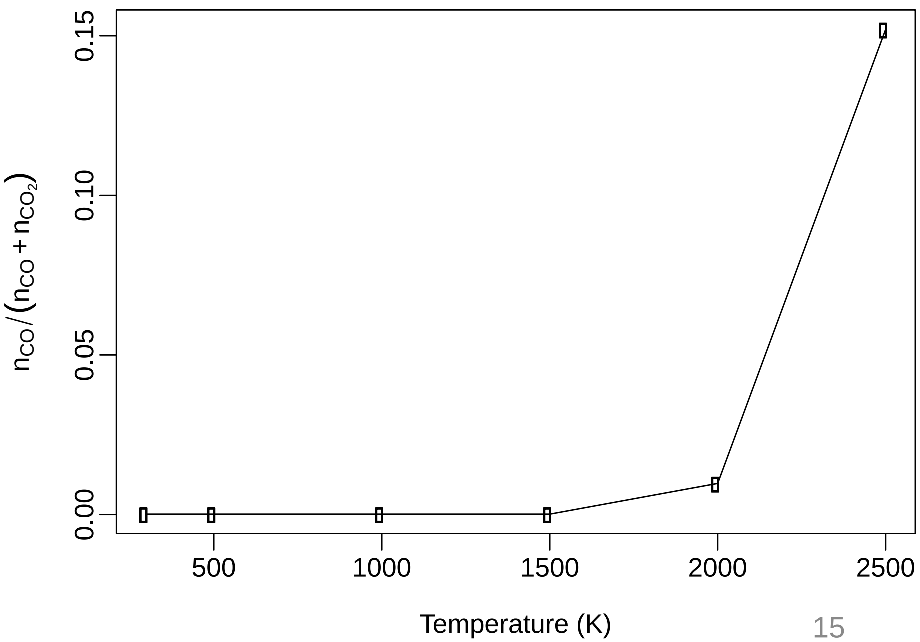
$$766 = \frac{(1 - n_{CO})(3.10 + 0.5n_{CO})^{1/2}}{n_{CO}(0.05 + 0.5n_{CO})^{1/2}}$$

Solution:

$$n_{CO} = 0.0097 \text{ mole}$$

$$n_{CO_2} = 0.9903 \text{ mole}$$

$$n_{O_2} = 0.0549 \text{ mole}$$



Soot

- Also goes by the name of black carbon (BC), elemental carbon (EC), light-absorbing carbon (LAC, but this also includes “brown carbon”)
- Absorbs solar radiation
- Processes of formation:
  - molecular growth by chemical reactions (polymerization of PAHs)
  - coagulation of PAH *i*-mers

Soot formation

In the following stoichiometric equation for incomplete combustion,

$$\mathrm{C_xH_y} + \alpha \mathrm{O_2} \rightarrow 2\alpha \mathrm{CO} + \frac{y}{2}\mathrm{H_2} + (x - 2\alpha)\mathrm{C_s}$$

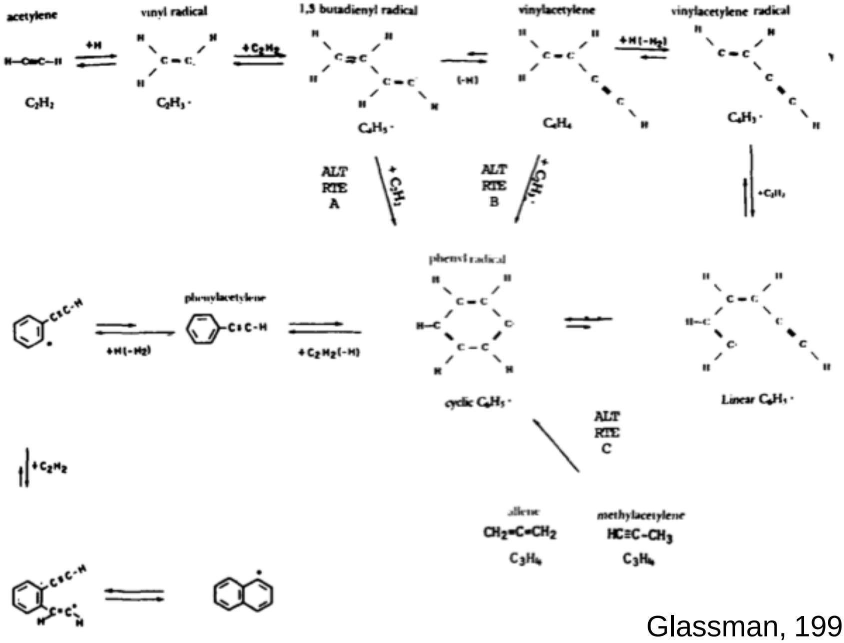
C_s is the soot formed and $(x/2\alpha)$ is the C/O (carbon to oxygen) molar ratio.

- When $C/O = 1$ $(x = 2\alpha)$, all of the carbon will be converted to CO.
- When $C/O < 1$ $(x < 2\alpha)$, there will be excess oxygen to convert CO to CO_2.
- When $C/O > 1$ $(x > 2\alpha)$, then soot will start forming.

In reality:

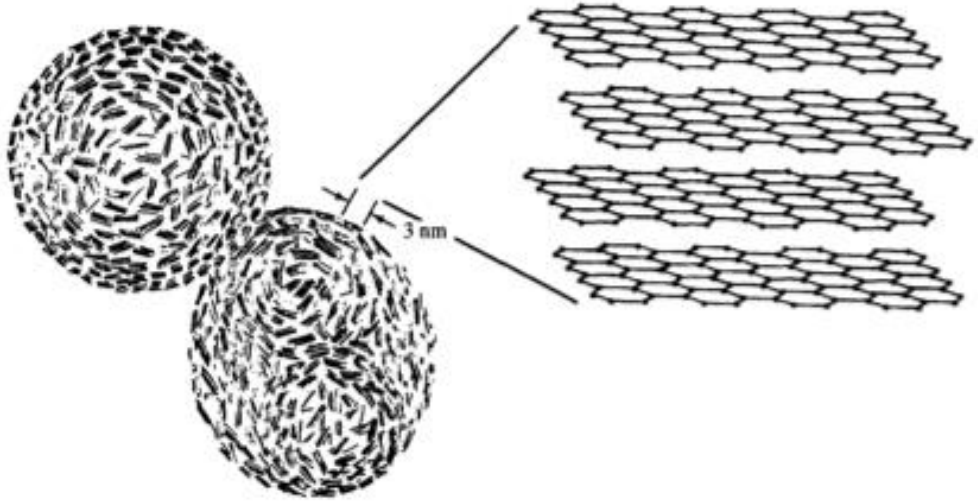
- Both CO and CO_2 are formed in the combustion even at low C/O ratios.
- Soot formation observed at low C/O ratios (close to 0.5; Wagner, 1981).
- Increasing temperature inhibits onset of soot formation.

Viewed by High-Resolution Transmission Electron Microscopy (HR-TEM)



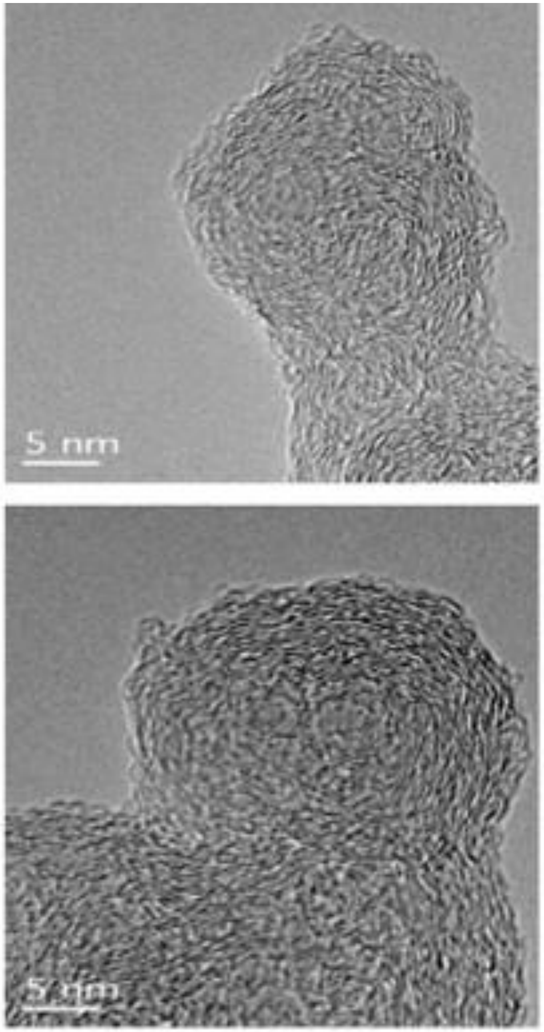
Glassman, 1998

FIG. 13a. General mechanisms for soot formation.

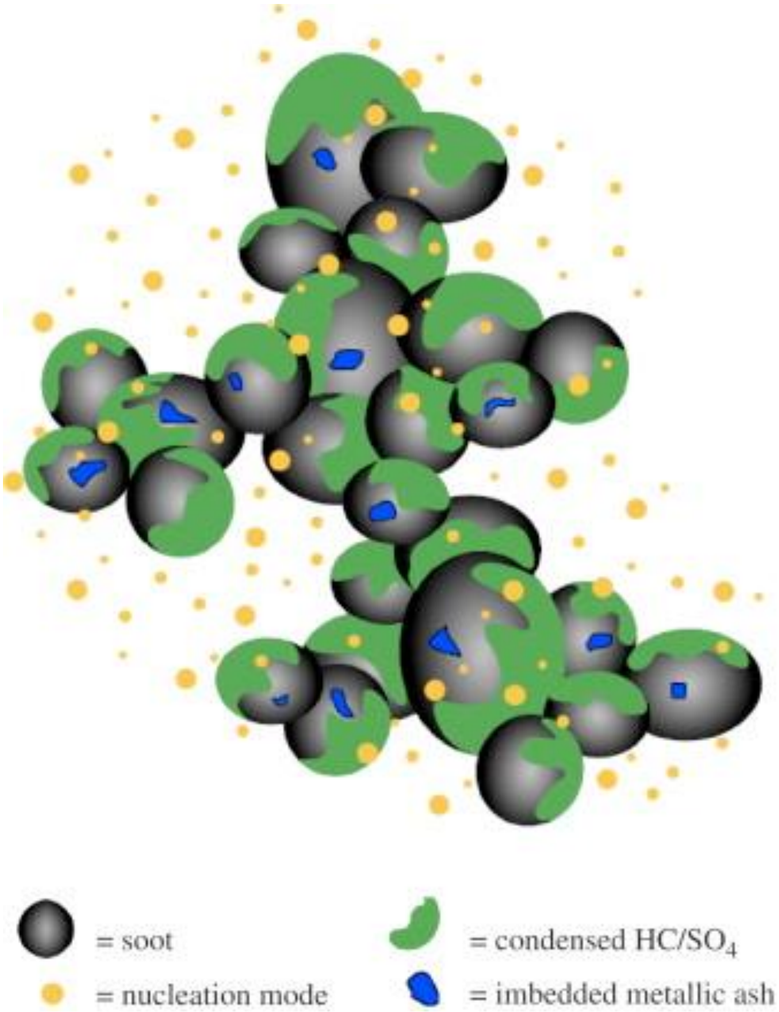


Seinfeld and Pandis, 2006

FIGURE 14.1 Schematic of soot microstructure.



Vander Wal, *Carbon*, 2007



Maricq, J. Aerosol Sci., 2007

Black carbon is almost never emitted by itself:

- Coated with lubricants and unburnt fuel
- Provides surfaces for rapid condensation of gases (organic compounds, sulfuric acid)

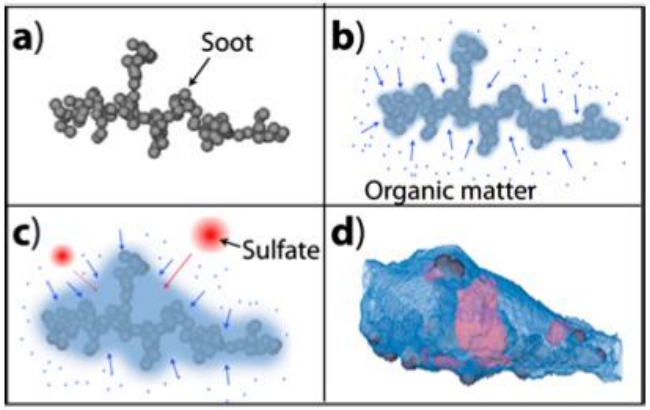


Figure 5. Presumed mixing processes (from Figure 5a to 5d) of soot, OM, and sulfate in the atmosphere for the particle shown in Figure 1a. (a) Aggregated soot without coating. (b) Condensation of OM onto the surface of the soot. (c) Coagulation of sulfate aerosol particles onto the particle. OM fills the spaces between the soot branches. (d) Observed particle using ET. Black, blue, and red indicate soot, OM, and sulfate, respectively.

Adachi et al., J. Geophys. Res., 201

Oxides of nitrogen (NO_x)

Recall that nitrogen is introduced during combustion with air:

$$C_xH_y + \left(x + \frac{y}{4}\right)(O_2 + \frac{79}{21}N_2)$$
$$\rightarrow xCO_2 + \frac{y}{2}H_2O + \left(x + \frac{y}{4}\right)\frac{79}{21}N_2$$

Thermal NOx

Extended Zeldavich mechanism (1946):

$$N_2 + O \rightleftharpoons NO + N$$
$$N + O_2 \rightleftharpoons NO + O$$
$$N + OH \rightleftharpoons NO + H$$

Overall:

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

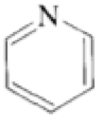
Conversion to NO_2:

$$NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$$

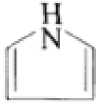
90% of NOx emitted as NO (Cooper and Alley, 2006).

Fuel NOx

$$RN \xrightarrow{\text{oxidant}} NO$$



pyridine



pyrrole

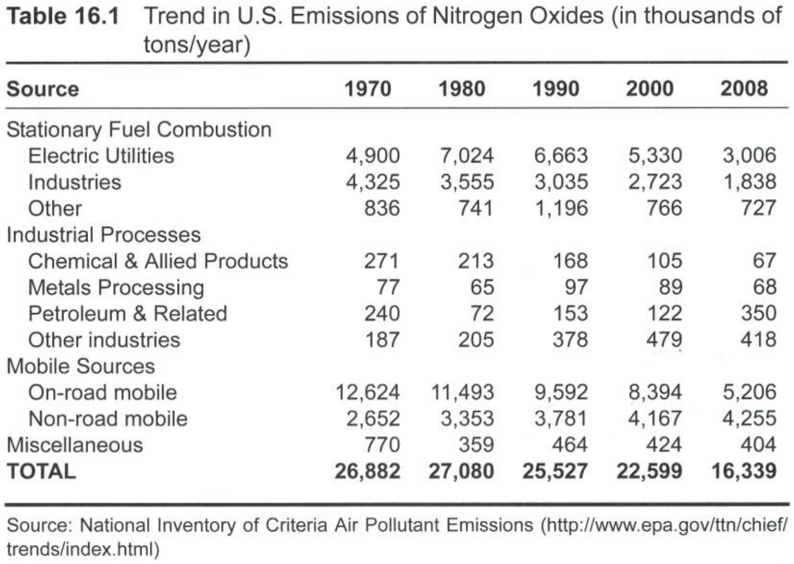


Table 16.1 Trend in U.S. Emissions of Nitrogen Oxides (in thousands of tons/year)

Source	1970	1980	1990	2000	2008
Stationary Fuel Combustion					
Electric Utilities	4,900	7,024	6,663	5,330	3,006
Industries	4,325	3,555	3,035	2,723	1,838
Other	836	741	1,196	766	727
Industrial Processes					
Chemical & Allied Products	271	213	168	105	67
Metals Processing	77	65	97	89	68
Petroleum & Related	240	72	153	122	350
Other industries	187	205	378	479	418
Mobile Sources					
On-road mobile	12,624	11,493	9,592	8,394	5,206
Non-road mobile	2,652	3,353	3,781	4,167	4,255
Miscellaneous	770	359	464	424	404
TOTAL	**26,882**	**27,080**	**25,527**	**22,599**	**16,339**

Source: National Inventory of Criteria Air Pollutant Emissions (http://www.epa.gov/ttn/chief/trends/index.html)

NO_x formation as a function of equivalence ratio

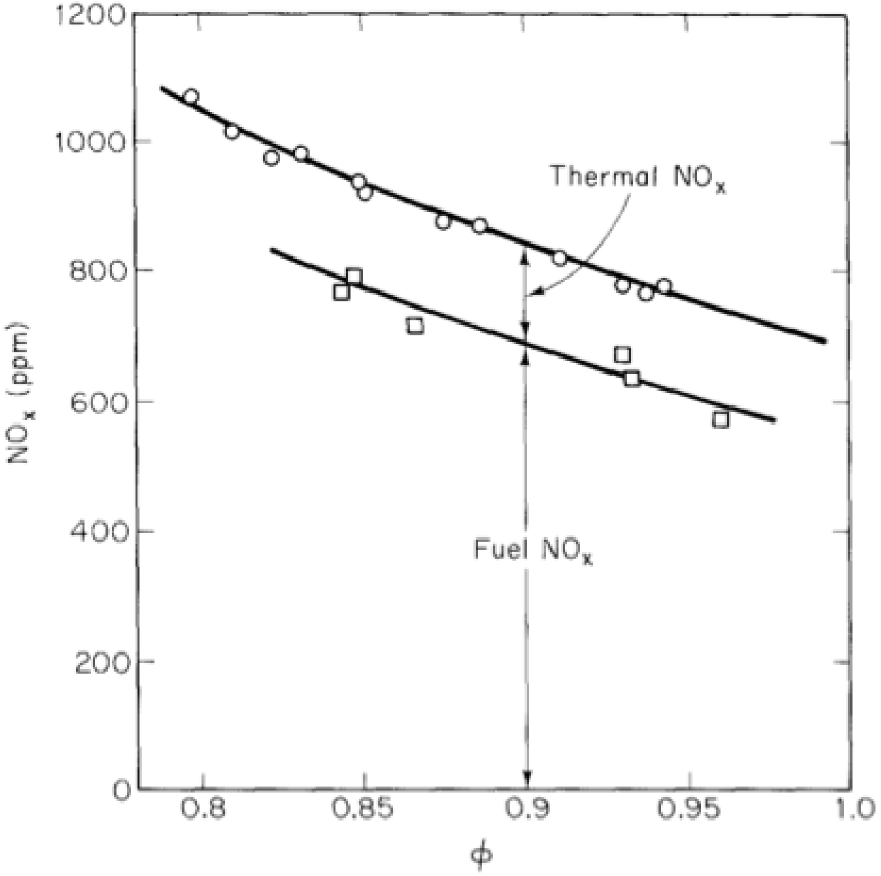


Figure 3.4 Contributions of thermal-NO_x and fuel-NO_x to total NO_x emissions in the laboratory pulverized coal combustion experiments of Pershing and Wendt (1977). Reprinted by permission of The Combustion Institute.

Flagan and Seinfeld, 1988

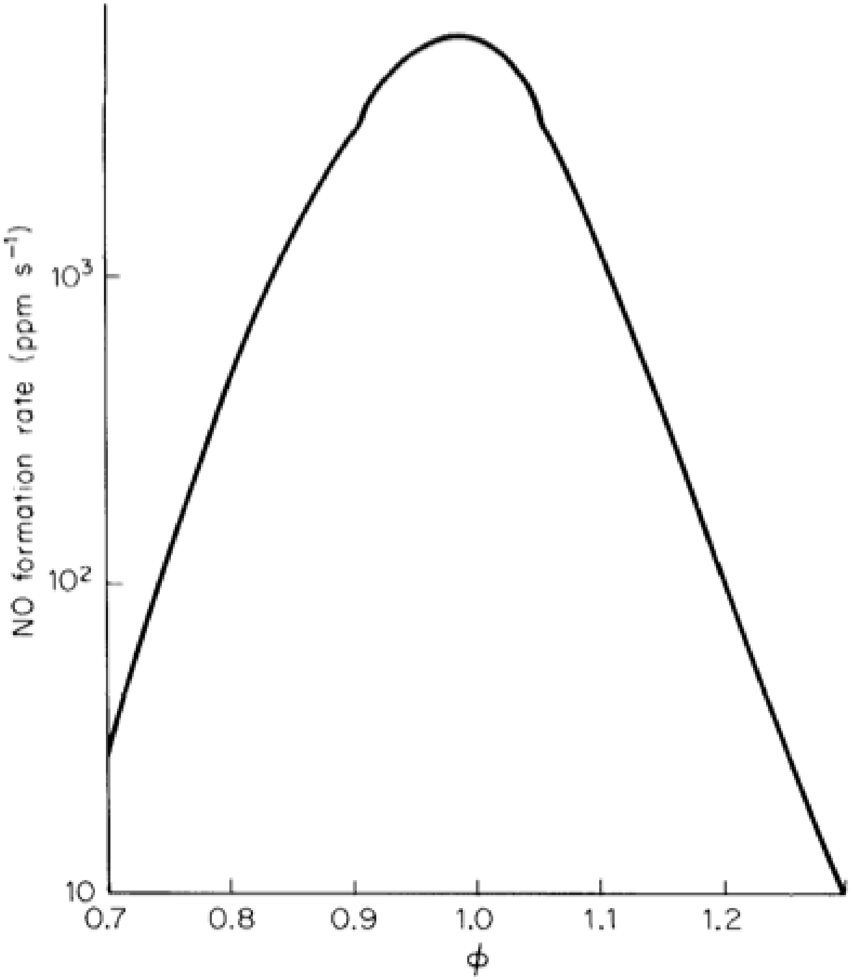


Figure 3.1 Variation of the initial NO formation rate with equivalence ratio for adiabatic combustion of kerosene with composition $CH_{1.8}$.

Sulfur dioxide (SO_2)

- S occurs in fuels as pyruvate, sulfides
- In coal:
  - – inorganic
    - iron pyrite (FeS_2)
    - occurs as discrete particles; washable
  - – organic
    - chemically bound

SO_2 Stack emissions from metal smelters

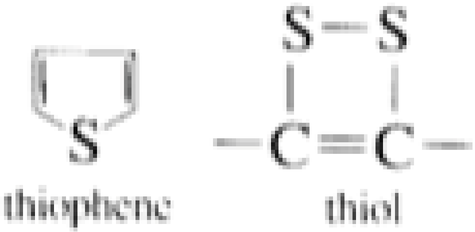
Norilsk (Russia)
2% of world-wide SO_2 emissions (>2 Mio t/year)

Pyrite: $4\,FeS_2 + 11\,O_2 \rightarrow 2\,Fe_2O_3 + 8\,SO_2$

Sphallerite: $2\,ZnS + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2$

Cinnabar: $HgS + O_2 \rightarrow Hg + SO_2$

slide by Stefan Reimann



Flagan and Seinfeld, 1988

SO_2 formation

SO_2 formation through SO pathway:

$$SO + O_2 \rightarrow SO_2 + O$$
$$SO + OH \rightarrow SO_2 + H$$

Overall reaction:

$$S + O_2 \rightarrow SO_2$$

Example 2.2 from Flagan and Seinfeld, 1988

Consider a Pittsburgh seam coal that contains 77.2% C, 5.2% H, 1.2% N, 2.6% S, 5.9% 0, and 7.9% ash by weight. The molar composition may be determined by dividing each of the mass percentages by the atomic weight of the constituent. For convenience in stoichiometric calculations, the composition is then normalized with respect to carbon (see Table).

Chemical formula normalized to a unit of carbon is $CH_{0.808}N_{0.013}S_{0.013}O_{0.057}$.

We can write the stoichiometric equation containing minor species such as ash and oxygen in the fuel:

$$\begin{aligned} &CH_{0.808}N_{0.013}S_{0.013}O_{0.057} + \alpha(O_2 + 3.78N_2) \\ &\quad \rightarrow CO_2 + 0.404H_2O + 0.013SO_2 + (3.78\alpha + 0.0065)N_2 \end{aligned}$$

where

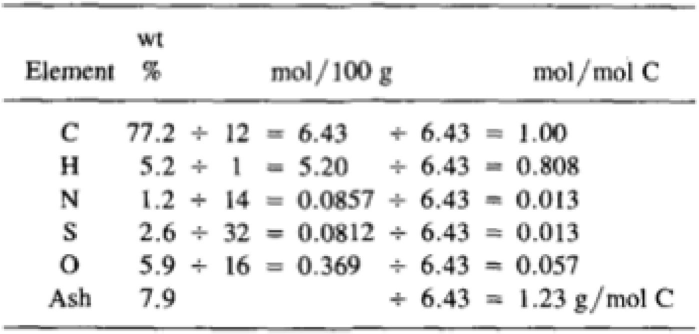
$$\alpha = 1 + 0.808/4 + 0.013 - 0.057/2 = 1.19$$

The total number of moles of gaseous combustion products per mole of C is

$$n = 1 + 0.404 + 0.013 + 4.504$$

The composition of combustion products in mole fractions:

$$\begin{aligned} y_{CO_2} &= \frac{1}{5.921} = 0.169 = 16.9\% \\ y_{H_2O} &= \frac{0.404}{5.921} = 0.068 = 6.82\% \\ y_{SO_2} &= \frac{0.013}{5.921} = 0.00220 = 2200\,\text{ppm} \\ y_{N_2} &= \frac{4.504}{5.921} = 0.761 = 76.1\% \end{aligned}$$



Element	wt %	mol / 100 g	mol / mol C
C	77.2	÷ 12 = 6.43	÷ 6.43 = 1.00
H	5.2	÷ 1 = 5.20	÷ 6.43 = 0.808
N	1.2	÷ 14 = 0.0857	÷ 6.43 = 0.013
S	2.6	÷ 32 = 0.0812	÷ 6.43 = 0.013
O	5.9	÷ 16 = 0.369	÷ 6.43 = 0.057
Ash	7.9		÷ 6.43 = 1.23 g / mol C

Particulate matter

- Anthropogenic vs. Biogenic
- Primary (emitted as particles) vs secondary (emitted precursor gases form particles in the atmosphere)
  - fly ash
  - metals
  - soot
  - organic carbon
  - other material

SOURCES

Combustion

- Anthropogenic (fossil fuel and burning of biomass)
- Biogenic (natural burning of biomass)

Emission parameters

Emission products formed depends on several factors:

- Fuel type
  - solid, liquid, gas
- Fuel composition
  - determines reaction pathways
- Flame type
  - determines local combustion environment
- Operating temperature (heterogeneous spatial distribution)
  - changes equilibrium and kinetic rate constants
- Air/fuel ratio
  - governs stoichiometry

The quantity of emission is dependent on the energy content of the fuel (how much fuel must be consumed to produce a fixed amount of energy).

Gas

- Simplest class of fuels
- Natural gas: mostly methane (CH_4) and ethane (C_2H_6)
  - found in underground reservoirs of porous rocks, alone or mixed with petroleum
- Other gases: C_1-C_5 e.g., propane (C_3H_8), butane (C_4H_{10})

modern natural gas-burning plant in Ohio, U.S.
source: NPR

Solid fuels

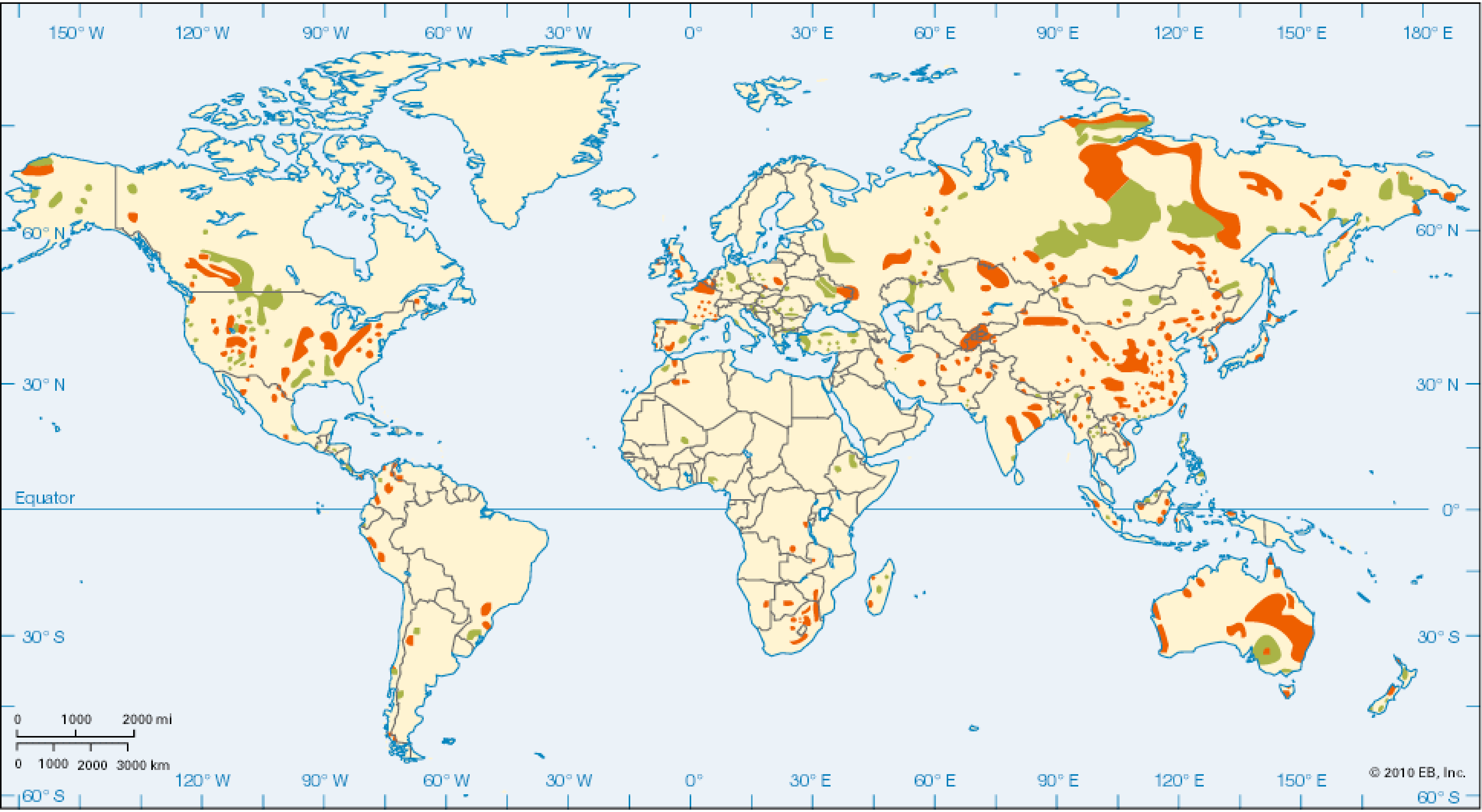
- Can include biomass and coal
- Composition varies more widely than other fuels

Burning wood

Coal

Coal

- Compact, stratified mass of decayed vegetation
  - variable composition (“organic rock”)
  - characterized by “rank”, indicating geological age—or the degree to which the organic matter has been transformed from cellulose to graphitic structure
- Often pulverized (formed into powder) and burned somewhat similarly to heavy fuel oils.
- Major emission products: SO_2, CO_2, NO_x, BC
- “Clean coal technology”
  - collection of methods to target removal of SO_2 and CO_2
  - may include: desulfurization (e.g., by washing) prior to burning; capturing of emissions post-burning
- There are various types of coal which vary in carbon and sulfur content, among other elements.



Major Coal Deposits of the World

🟧 Anthracite and Bituminous Coal

🟩 Lignite

source: *Encyclopædia Britannica, Inc.*

Gasoline and diesel

- both are mixture of hydrocarbons processed from petroleum
- gasoline
  - predominantly C_4-C_{12} with boiling point of 25-220°C
  - spark ignition
  - higher CO and VOC emissions
- diesel
  - typically heavier and less volatile than gasoline
  - predominantly C_9-C_{28} with boiling point of 160-390°C
  - compressed to autoignition temperature
  - lower AFR, higher pressures and temperatures
  - higher NO_x and soot emissions

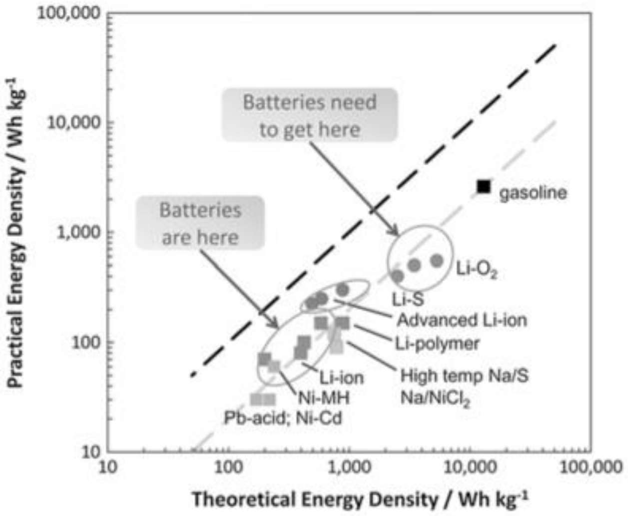


Fig. 1.2 A plot of theoretical specific energy of various rechargeable battery systems versus their practical specific energy compared to that of gasoline. Reprinted from Thackeray et al. (2012), copyright The Royal Society of Chemistry

Battin-Leclerc et al., 2013

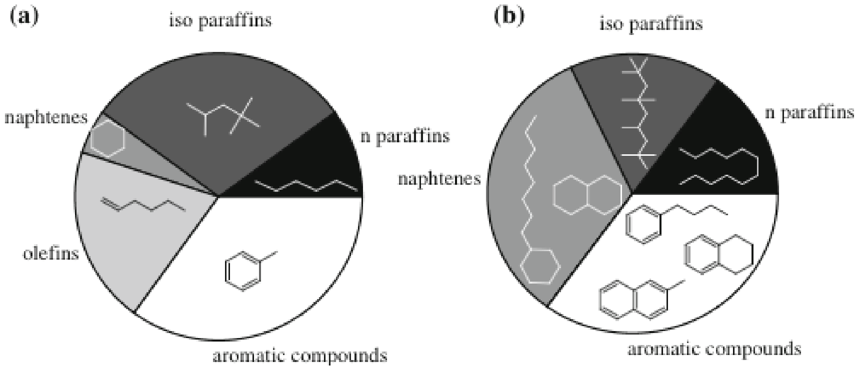
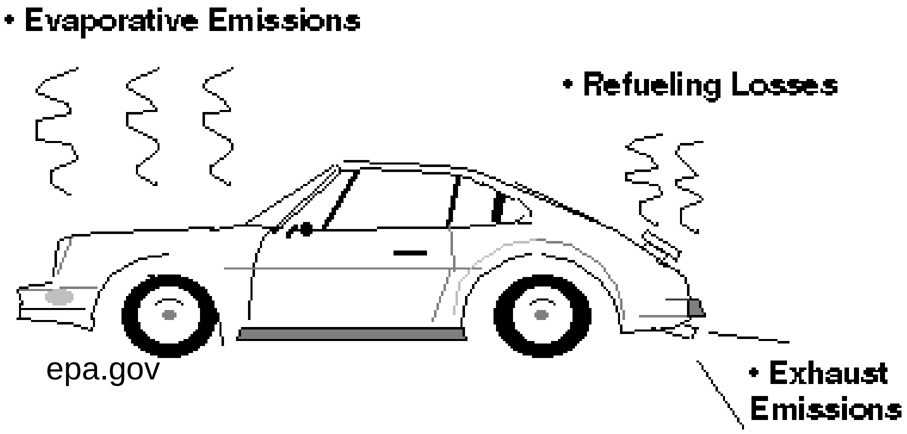


Fig. 1.3 Typical composition of (**a**) European gasoline (Guibet 1999) and of (**b**) a US diesel duel (Pitz and Mueller 2011), and possible model compounds to represent the component families (for diesel fuel, models are not available for all presented model compounds)

Battin-Leclerc et al., 2013

Automotive emissions

http://www.greenoptimistic.com/



epa.gov

Primary organic (and elemental) carbon emissions

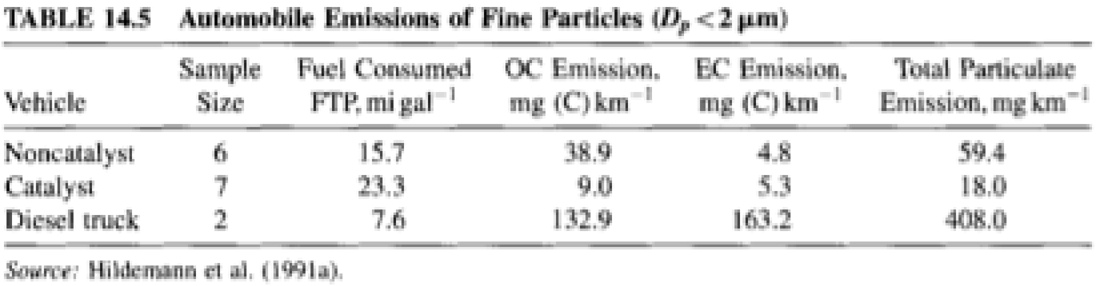


TABLE 14.5 Automobile Emissions of Fine Particles ($D_p < 2\ \mu m$)

Vehicle	Sample Size	Fuel Consumed FTP, mi gal^{-1}	OC Emission, mg (C) km^{-1}	EC Emission, mg (C) km^{-1}	Total Particulate Emission, mg km^{-1}
Noncatalyst	6	15.7	38.9	4.8	59.4
Catalyst	7	23.3	9.0	5.3	18.0
Diesel truck	2	7.6	132.9	163.2	408.0

Source: Hildemann et al. (1991a).

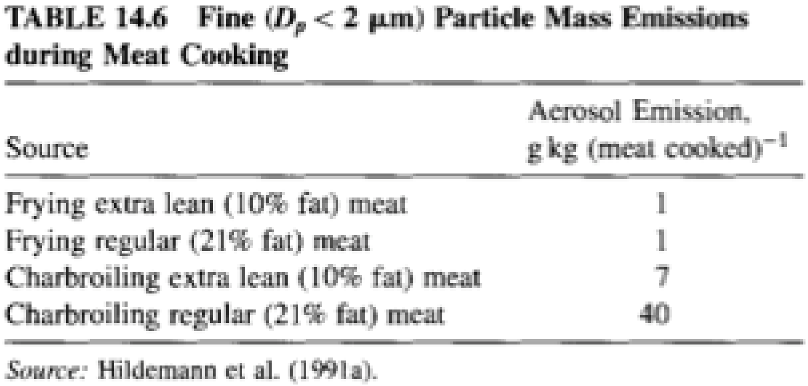


TABLE 14.6 Fine ($D_p < 2\ \mu m$) Particle Mass Emissions during Meat Cooking

Source	Aerosol Emission, g kg (meat cooked)$^{-1}$
Frying extra lean (10% fat) meat	1
Frying regular (21% fat) meat	1
Charbroiling extra lean (10% fat) meat	7
Charbroiling regular (21% fat) meat	40

Source: Hildemann et al. (1991a).

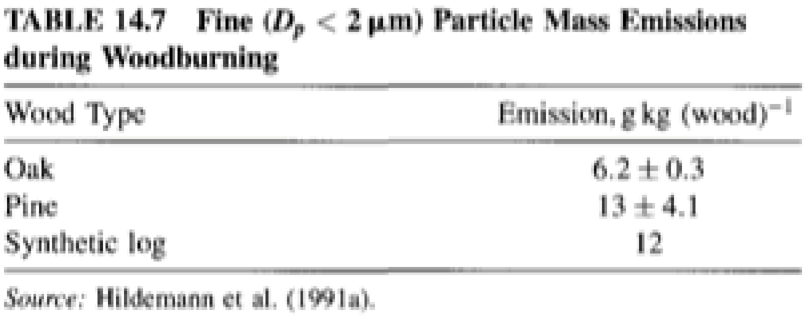


TABLE 14.7 Fine ($D_p < 2\ \mu m$) Particle Mass Emissions during Woodburning

Wood Type	Emission, g kg (wood)$^{-1}$
Oak	6.2 ± 0.3
Pine	13 ± 4.1
Synthetic log	12

Source: Hildemann et al. (1991a).

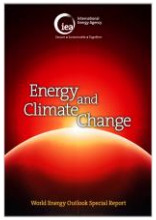
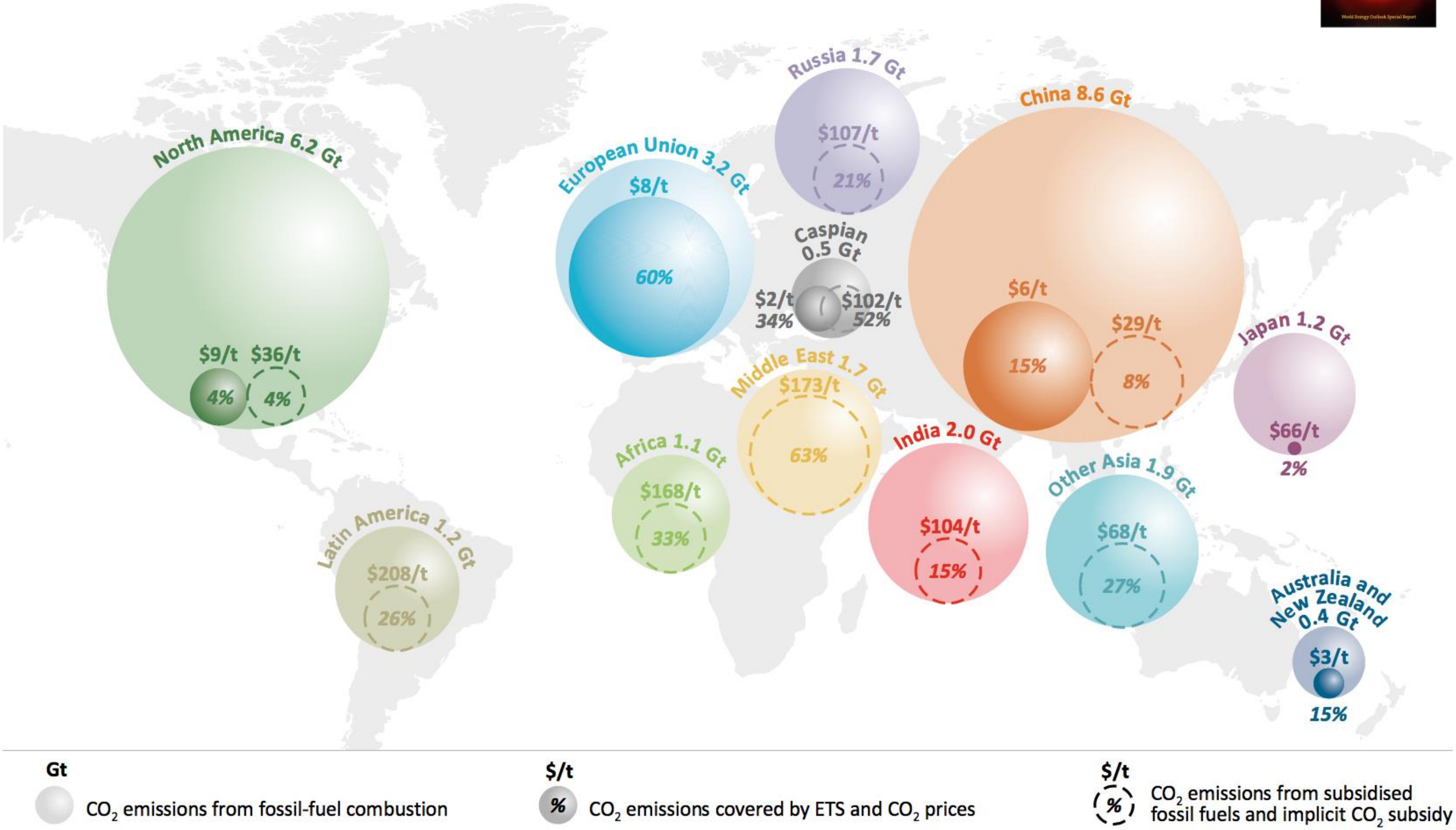
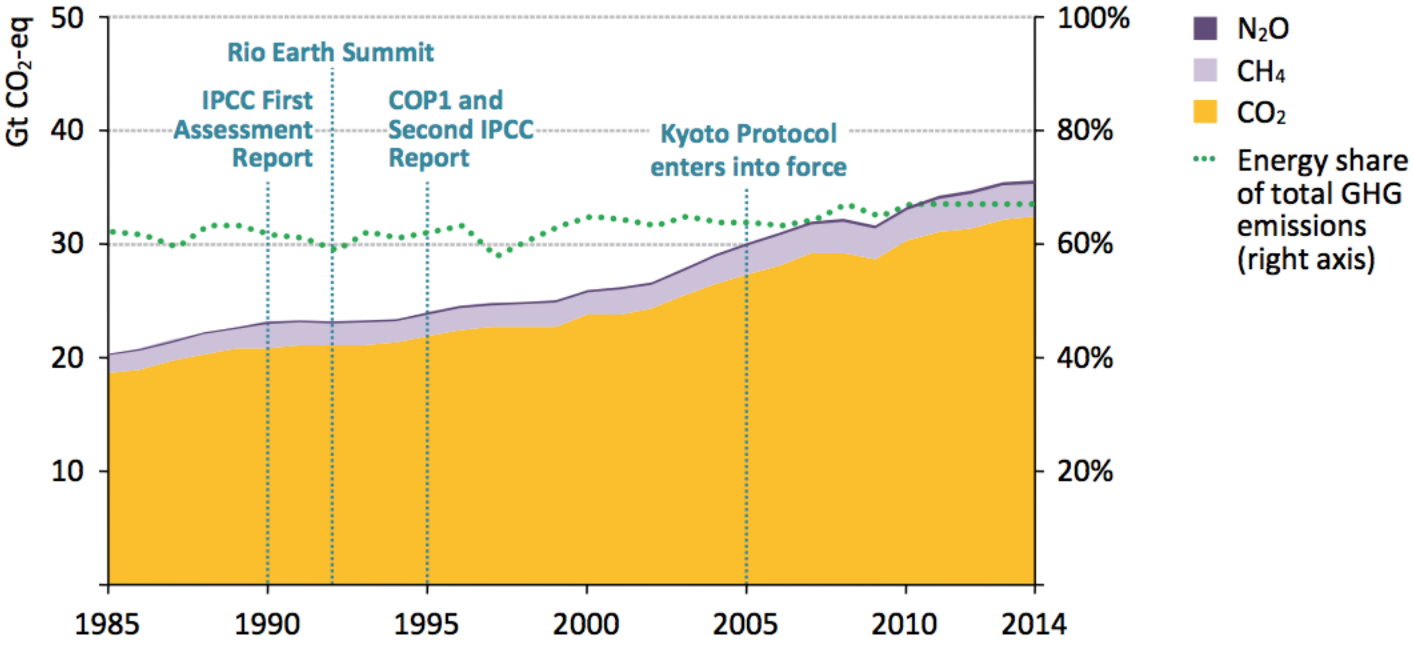


Figure 1.2 ▷ Energy-related CO_2 emissions in selected regions, 2014



Notes: The implicit CO_2 subsidy is calculated as the ratio of the economic value of those subsidies to the CO_2 emissions released from subsidised energy consumption. ETS = emissions trading scheme.

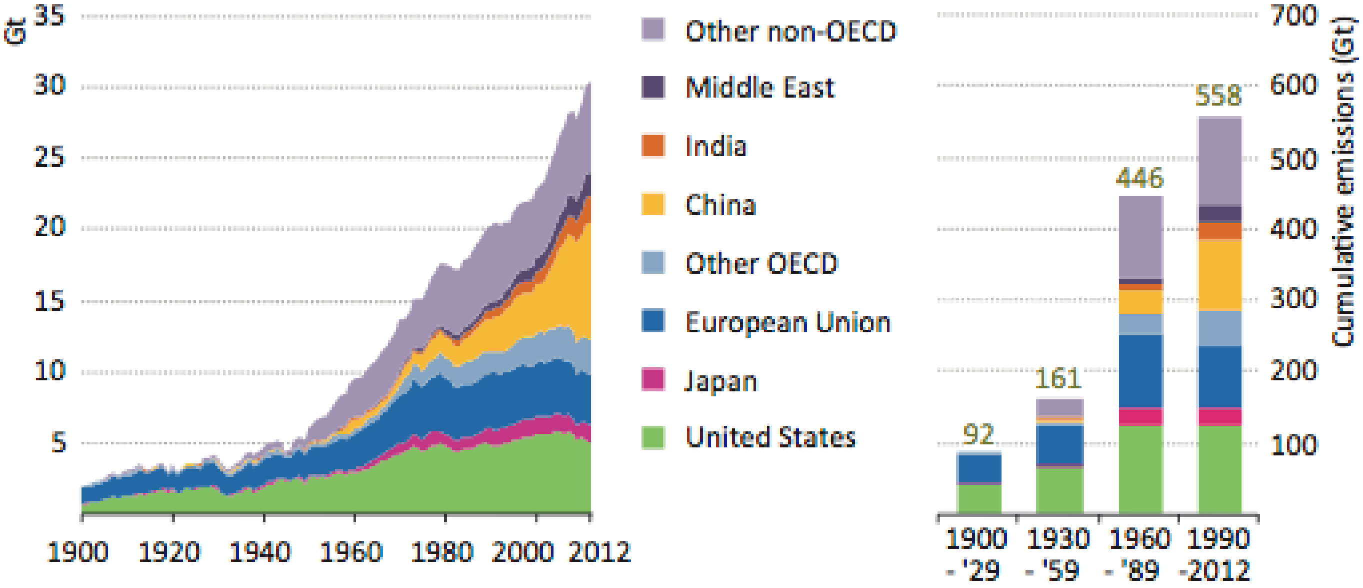
Figure 1.3 ▷ Global anthropogenic energy-related greenhouse-gas emissions by type



Notes: CO_2 = carbon dioxide, CH_4 = methane, N_2O = nitrous oxide. CH_4 has a global warming potential of 28 to 30 times that of CO_2, while the global warming potential of N_2O is 265 higher than that of CO_2.

Sources: IEA and EC/PBL (2014).

Figure 1.11 ▷ Energy-related CO_2 emissions by country



Sources: IEA databases and analysis; Boden *et al.*, (2013).

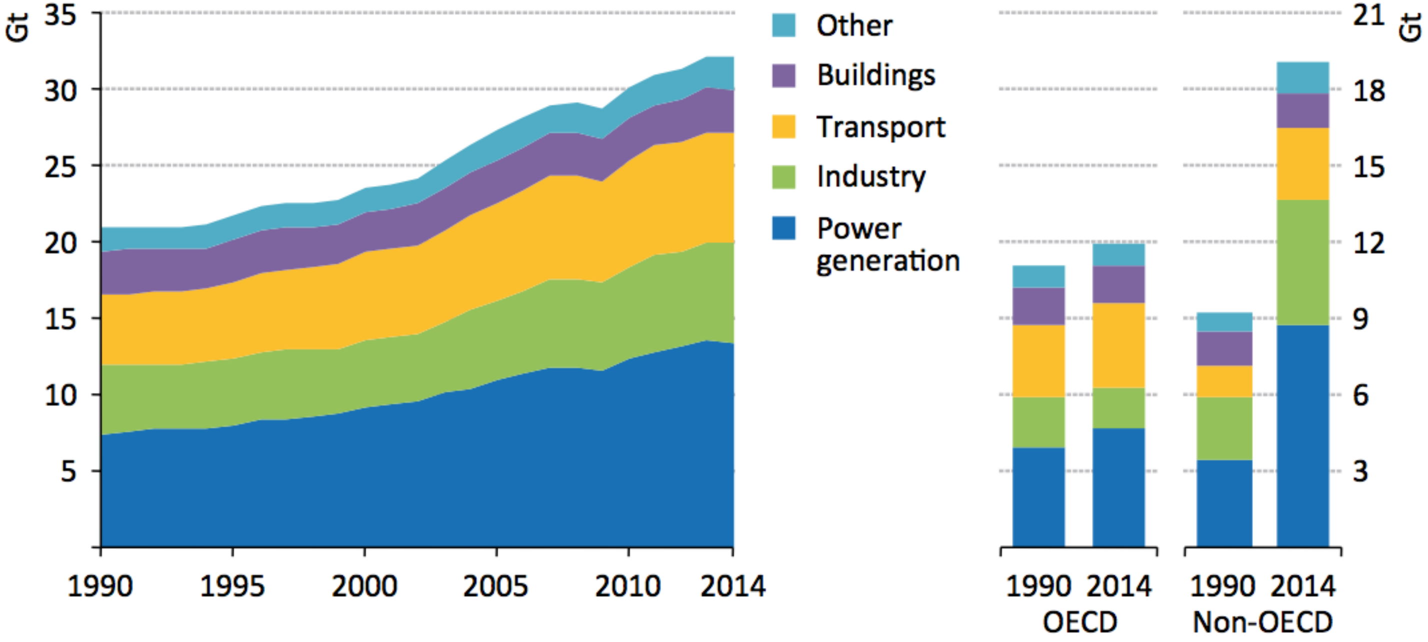
IEA, *World Outlook 2013*

Figure 1.4 ▷ **Cumulative energy-related CO_2 emissions by region**

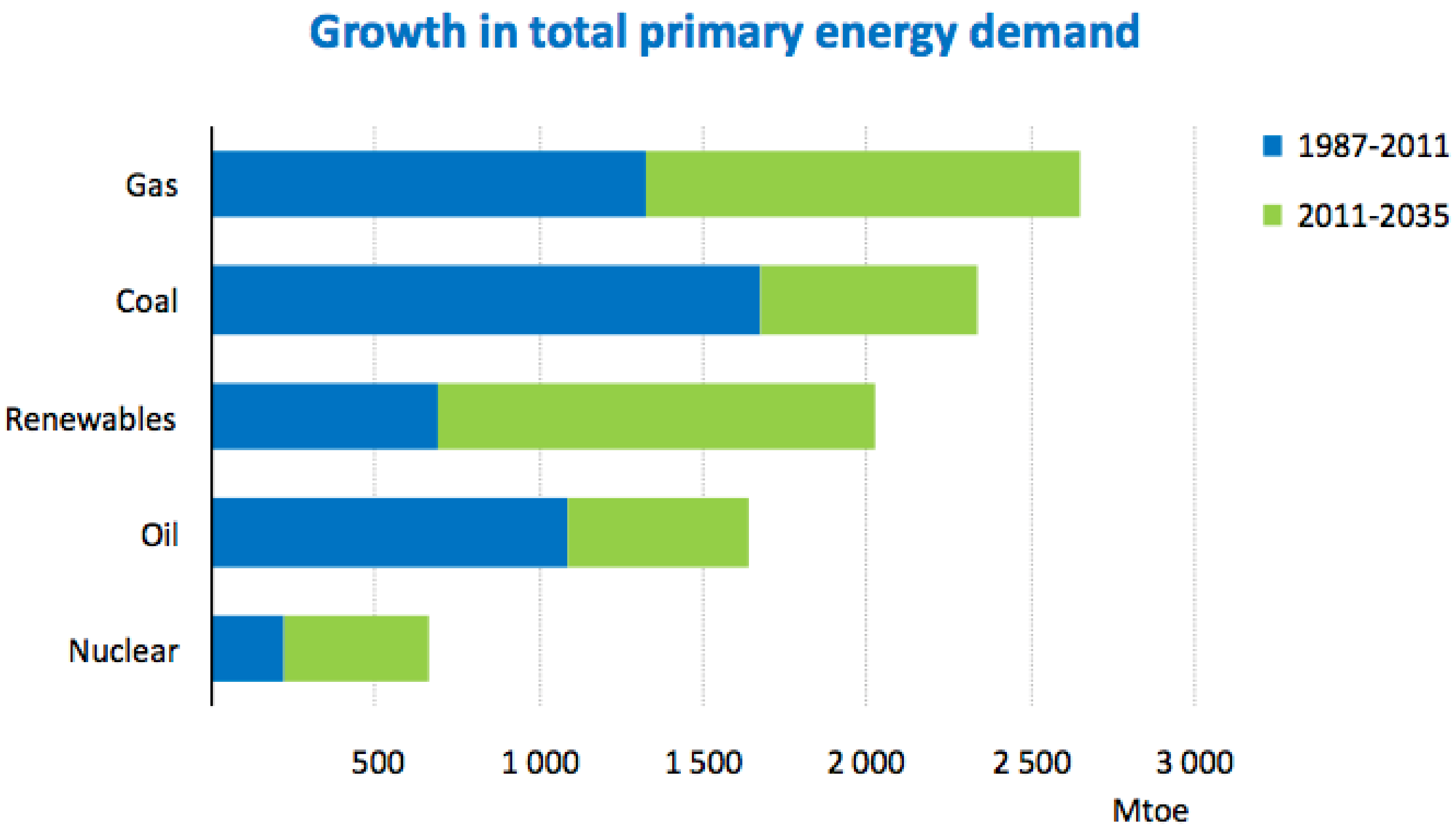
Notes: Emissions for the European Union prior to 2004 represent the combined emissions of its current member states. Emissions for Russia prior to 1992 represent emissions from the Union of Soviet Socialist Republics. Rest of world includes international bunkers.

Sources: Marland, Boden and Andres (2008) and IEA (2014a).

Figure 1.5 ▷ Global energy-related CO_2 emissions by sector and region



Notes: "Other" includes agriculture, non-energy use (except petrochemical feedstock), oil and gas extraction and energy transformation. International bunkers are included in the transport sector at the global level but excluded from the regional data.

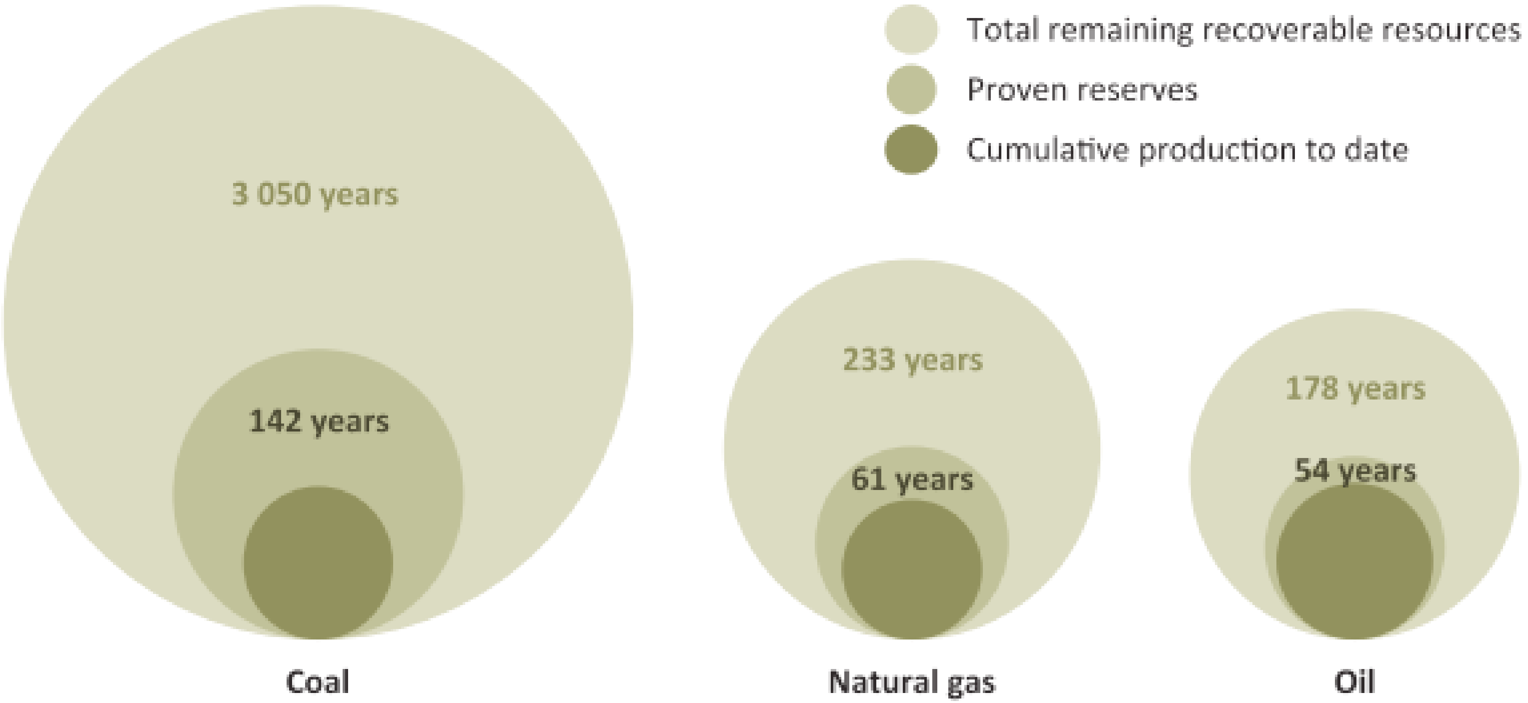


Growth in total primary energy demand

(Million tonnes of oil equivalent)

IEA, *World Outlook 2013*

Figure 2.10 ▻ Fossil energy resources by type



Notes: All bubbles are expressed as a number of years of production based on estimated production in 2013. The size of the bubble for total remaining recoverable resources of coal is illustrative and is not proportional to the others. The figure specifies the status of reserves for coal as of end-2011, and gas and oil as of end-2012. Sources: BGR (2012); O&GJ (2012); USGS (2000, 2012a and 2012b); IEA estimates and analysis.

IEA, *World Outlook 2013*

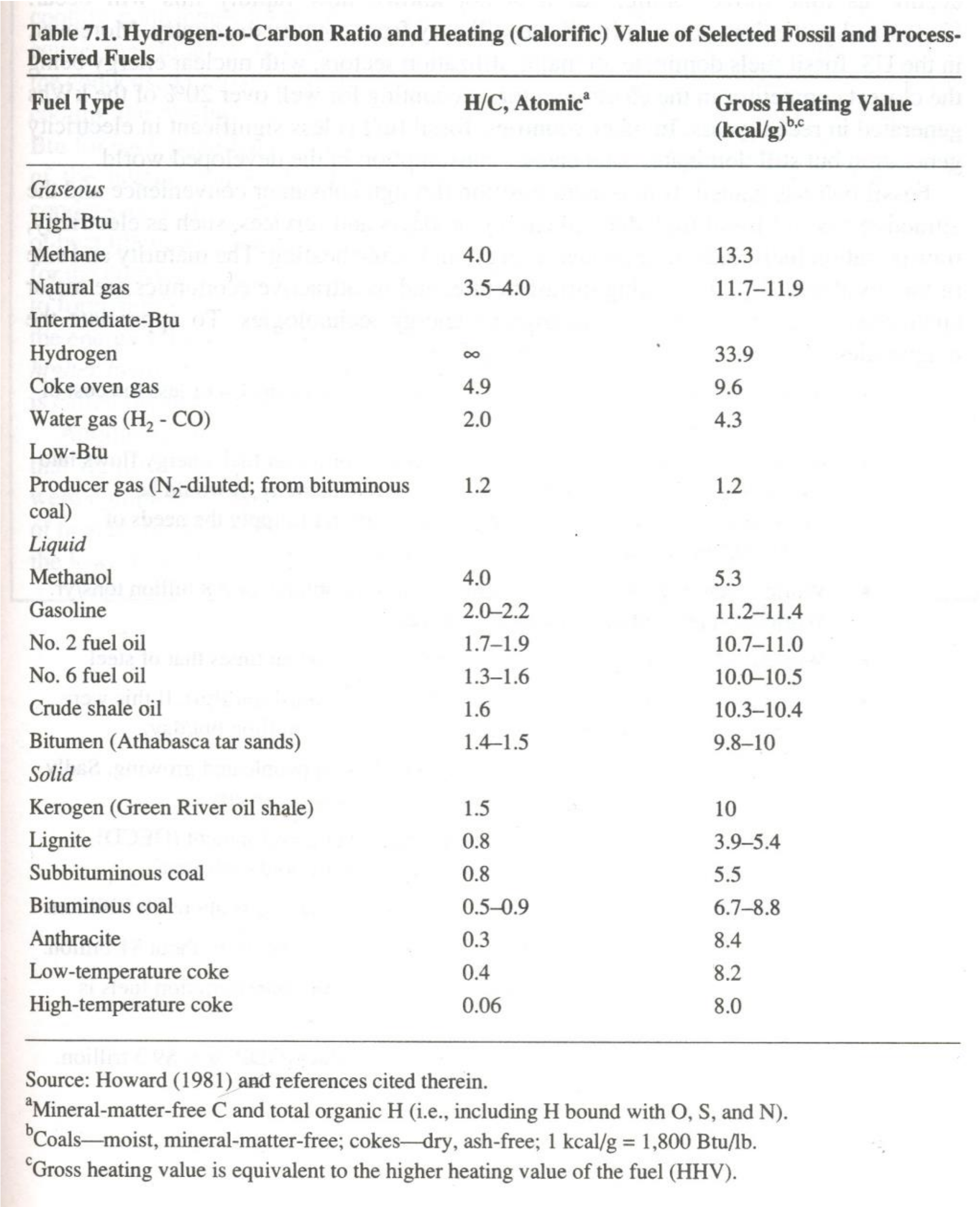


Table 7.1. Hydrogen-to-Carbon Ratio and Heating (Calorific) Value of Selected Fossil and Process-Derived Fuels

Fuel Type	H/C, Atomic[a]	Gross Heating Value (kcal/g)[b,c]
Gaseous		
High-Btu		
Methane	4.0	13.3
Natural gas	3.5–4.0	11.7–11.9
Intermediate-Btu		
Hydrogen	∞	33.9
Coke oven gas	4.9	9.6
Water gas (H_2 - CO)	2.0	4.3
Low-Btu		
Producer gas (N_2-diluted; from bituminous coal)	1.2	1.2
Liquid		
Methanol	4.0	5.3
Gasoline	2.0–2.2	11.2–11.4
No. 2 fuel oil	1.7–1.9	10.7–11.0
No. 6 fuel oil	1.3–1.6	10.0–10.5
Crude shale oil	1.6	10.3–10.4
Bitumen (Athabasca tar sands)	1.4–1.5	9.8–10
Solid		
Kerogen (Green River oil shale)	1.5	10
Lignite	0.8	3.9–5.4
Subbituminous coal	0.8	5.5
Bituminous coal	0.5–0.9	6.7–8.8
Anthracite	0.3	8.4
Low-temperature coke	0.4	8.2
High-temperature coke	0.06	8.0

Source: Howard (1981) and references cited therein.

[a] Mineral-matter-free C and total organic H (i.e., including H bound with O, S, and N).

[b] Coals—moist, mineral-matter-free; cokes—dry, ash-free; 1 kcal/g = 1,800 Btu/lb.

[c] Gross heating value is equivalent to the higher heating value of the fuel (HHV).

Tester et al., 2005

Thermodynamics of combustion based on chemical composition

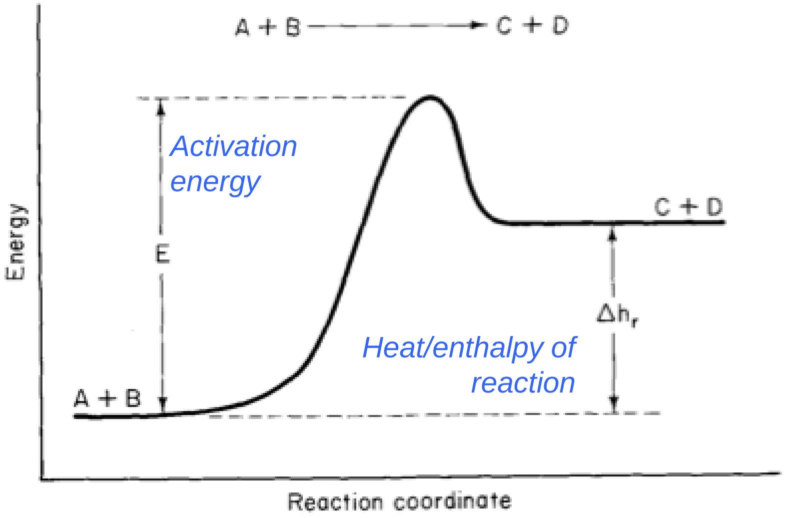


Figure 1.1 Energetics of an exchange reaction $A + B \rightarrow C + D$.

Flagan and Seinfeld (1988)

Change in enthalpy represents heat exchange and pressure-volume work under constant pressure.

$$\Delta H = Q_p$$

The enthalpy of reaction can be calculated as

$$\boxed{\Delta_{\text{rxn}} H^0 = \sum_{i \in \text{Products}} n_i \Delta_f H_i^0 - \sum_{i \in \text{Reactants}} n_i \Delta_f H_i^0}$$

- $\Delta_{\text{rxn}} H^0 > 0$: endothermic
- $\Delta_{\text{rxn}} H^0 < 0$: exothermic

Heat of combustion, $\Delta_c H^0$, is the energy (as heat) released when a substance undergoes complete combustion with oxygen under standard conditions (a hypothetical enthalpy of reaction). This is related to the heating value of the substance (heat released per unit mole or mass during combustion).

Exampe: methane

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$$

$$\begin{aligned}\Delta_c H^0 &= \left(2\Delta H^0_{\text{C=O}} + 2\cdot 2\Delta H^0_{\text{O-H}}\right) - \left(4\Delta H^0_{\text{C-H}} + 2\Delta H^0_{\text{O=O}}\right)\\ &= [2\cdot(-192)\,\text{kcal/mol} + 4\cdot(-110.6)\,\text{kcal/mol}] - [4\cdot(-98.7)\,\text{kcal/mol} + 2\cdot(-118.9)\,\text{kcal/mol}) -\\ &= -193.8\,\text{kcal/mol}\end{aligned}$$

$$\frac{1\,\text{mol CH}_4}{193.8\,\text{kcal}}\cdot\frac{1\,\text{mole CO}_2}{1\,\text{mole CH}_4}\cdot\frac{44.01\,\text{g CO}_2}{\text{mol CO}_2}\cdot\frac{1\,\text{kcal}}{4.184\text{kJ}} = 0.0543\,\text{g/kJ}$$

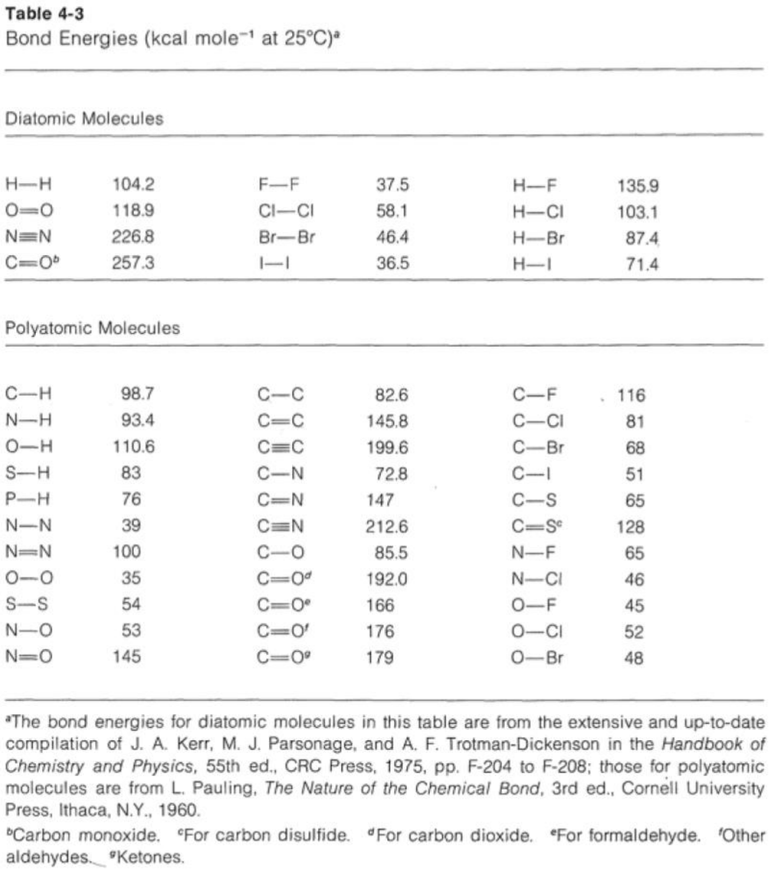


Table 4-3
Bond Energies (kcal mole⁻¹ at 25°C)[a]

Diatomic Molecules

H—H	104.2	F—F	37.5	H—F	135.9
O═O	118.9	Cl—Cl	58.1	H—Cl	103.1
N≡N	226.8	Br—Br	46.4	H—Br	87.4
C≡O[b]	257.3	I—I	36.5	H—I	71.4

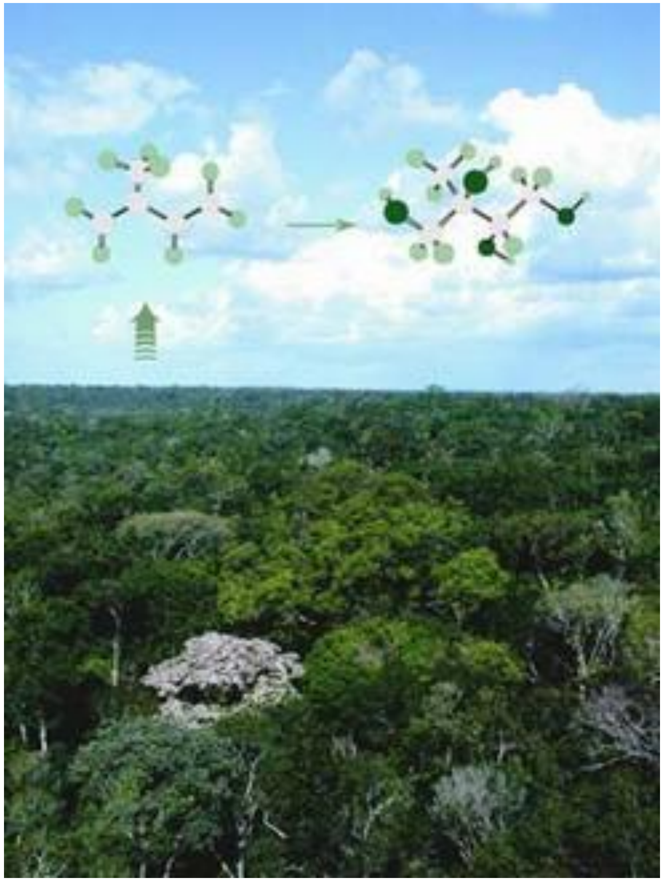
Polyatomic Molecules

C—H	98.7	C—C	82.6	C—F	116
N—H	93.4	C═C	145.8	C—Cl	81
O—H	110.6	C≡C	199.6	C—Br	68
S—H	83	C—N	72.8	C—I	51
P—H	76	C═N	147	C—S	65
N—N	39	C≡N	212.6	C═S[c]	128
N═N	100	C—O	85.5	N—F	65
O—O	35	C═O[d]	192.0	N—Cl	46
S—S	54	C═O[e]	166	O—F	45
N—O	53	C═O[f]	176	O—Cl	52
N═O	145	C═O[g]	179	O—Br	48

[a] The bond energies for diatomic molecules in this table are from the extensive and up-to-date compilation of J. A. Kerr, M. J. Parsonage, and A. F. Trotman-Dickenson in the *Handbook of Chemistry and Physics*, 55th ed., CRC Press, 1975, pp. F-204 to F-208; those for polyatomic molecules are from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

[b] Carbon monoxide. [c] For carbon disulfide. [d] For carbon dioxide. [e] For formaldehyde. [f] Other aldehydes. [g] Ketones.

Fields, Forests, Grasslands, etc.

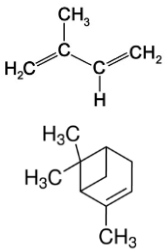


www.mpg.de

- Volatile organic compounds (VOCs) make up a large fraction of relevant emissions.
- VOCs can be oxidized to form organic particles in the atmosphere.

Biogenic hydrocarbon emissions

- Biological conversion of CO_2 to organic molecules
- Isoprene emission is light-dependent but monoterpenes are not necessarily
    - isoprene: temperature-dependent volatility
    - monoterpene: volatility and concentration (Henry's law)
    - differs in storage mechanism within the plant
- Vegetation type
    - Coniferous (pine): terpenes
    - Deciduous (oak): isoprene



Guenther et al., 1993

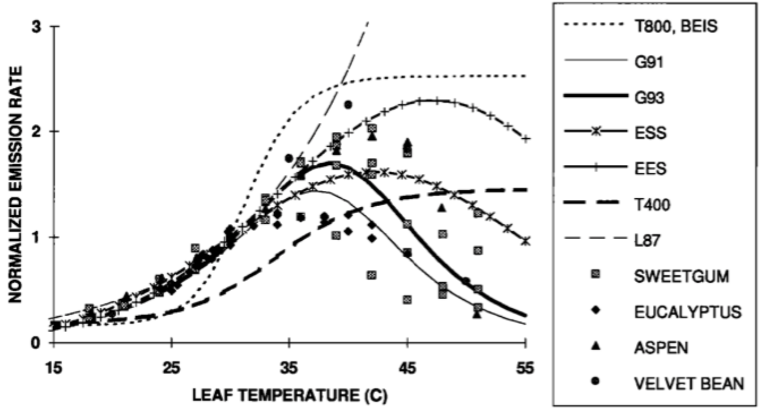
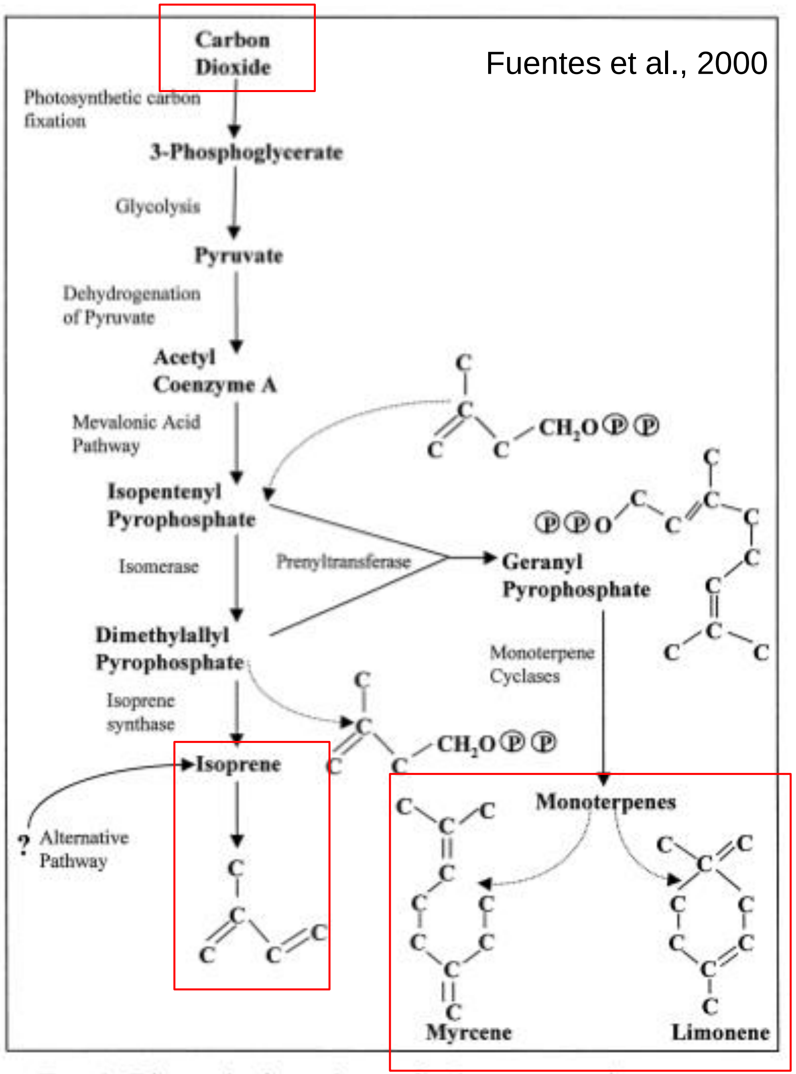


Fig. 3. Relationship between normalized isoprene emission rates and leaf temperatures observed for sweet gum, eucalyptus, aspen, and velvet beans (symbols) and simulated by eight of the isoprene emission models described in Table 1 (lines).



Fuentes et al., 2000

Fig. 1. Biosynthetic pathway for isoprene and monoterpene production in plants.

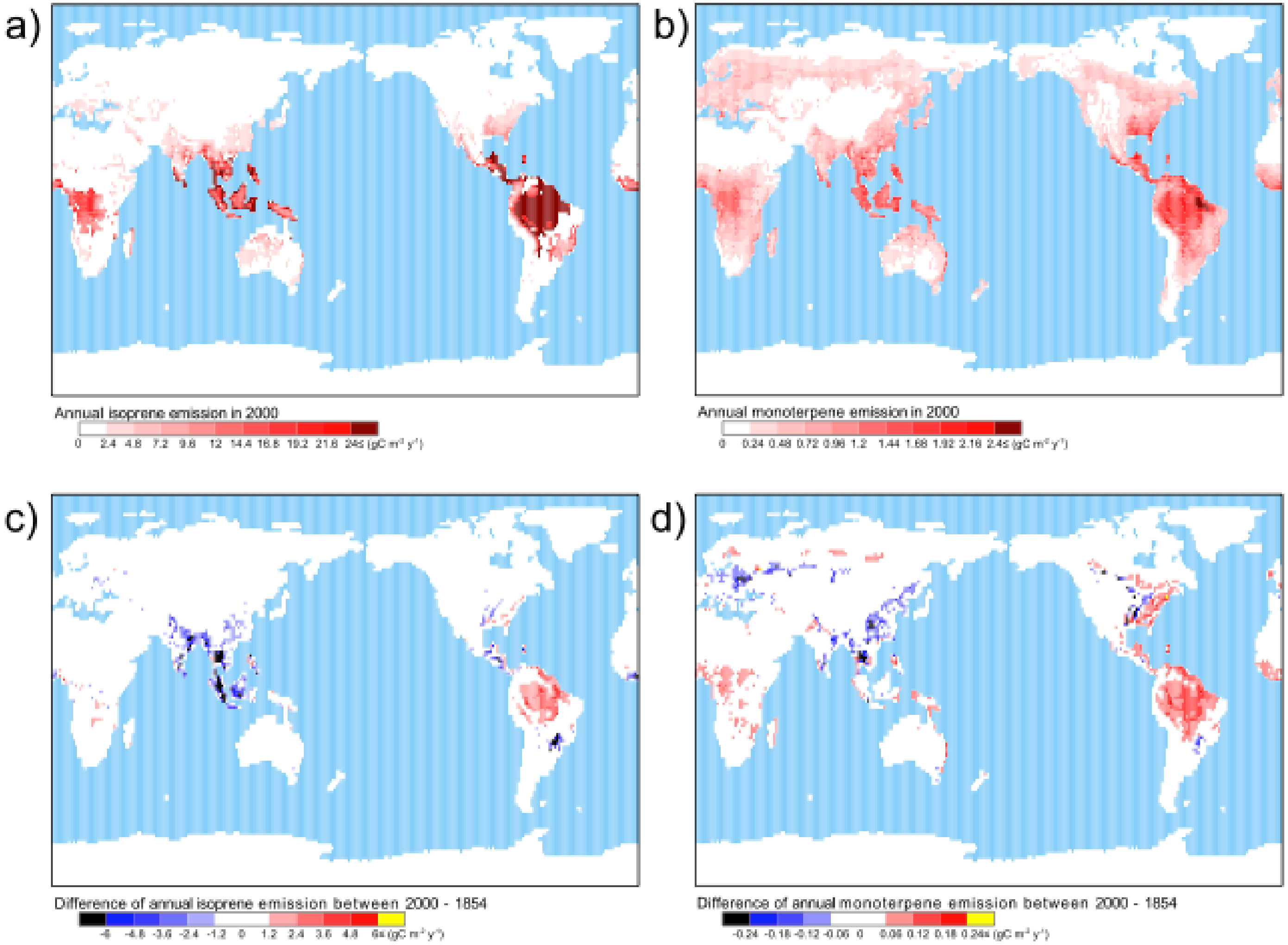


Fig. 7. Distribution of estimated annual global emissions (gC m^{-2} yr^{-1}) in 2000, and the differences between 2000 and 1854 for isoprene (**a** and **c**) and monoterpenes (**b** and **d**), respectively.

Tanaka et al. 2000

Burning of biomass

- Mixture of combustion and biogenic products
- Various burning conditions: flaming, smoldering (varies in temperature)
- Many possible fuel types

Bond et al., 2013

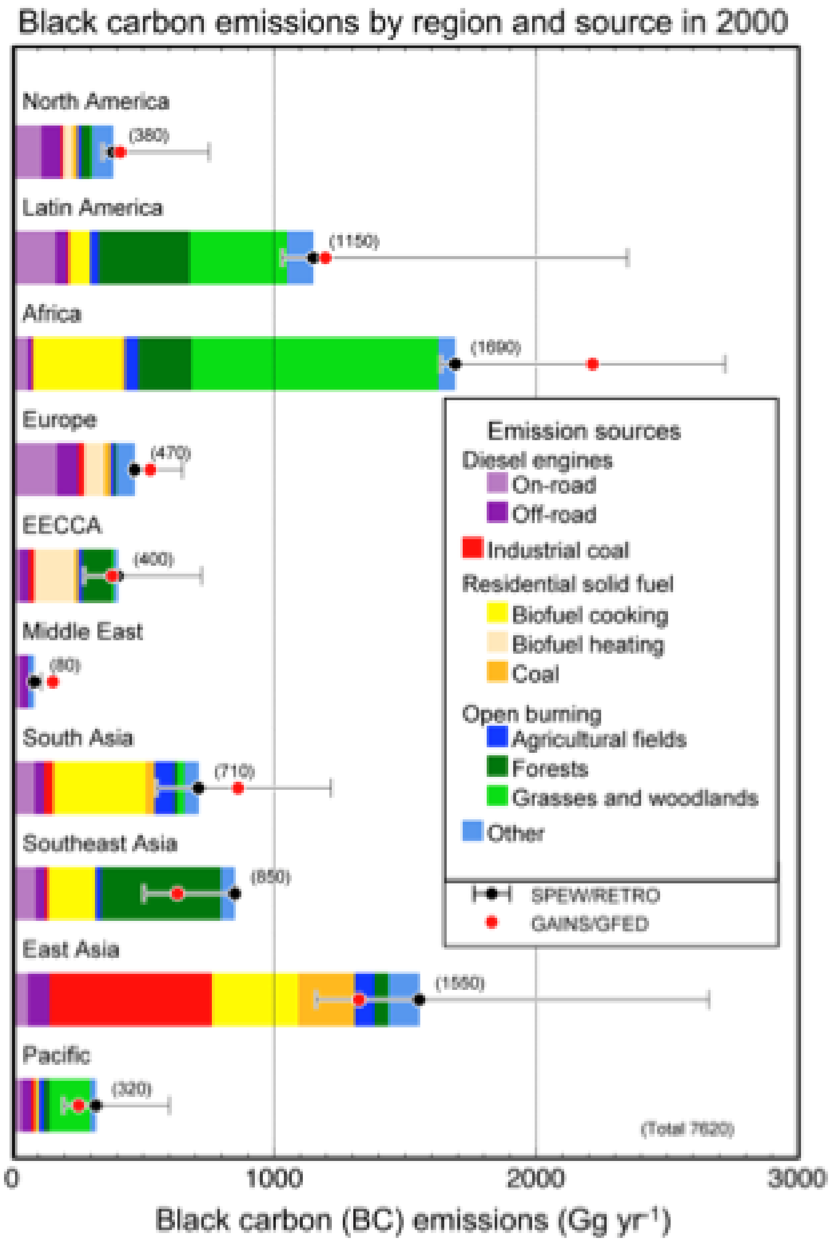
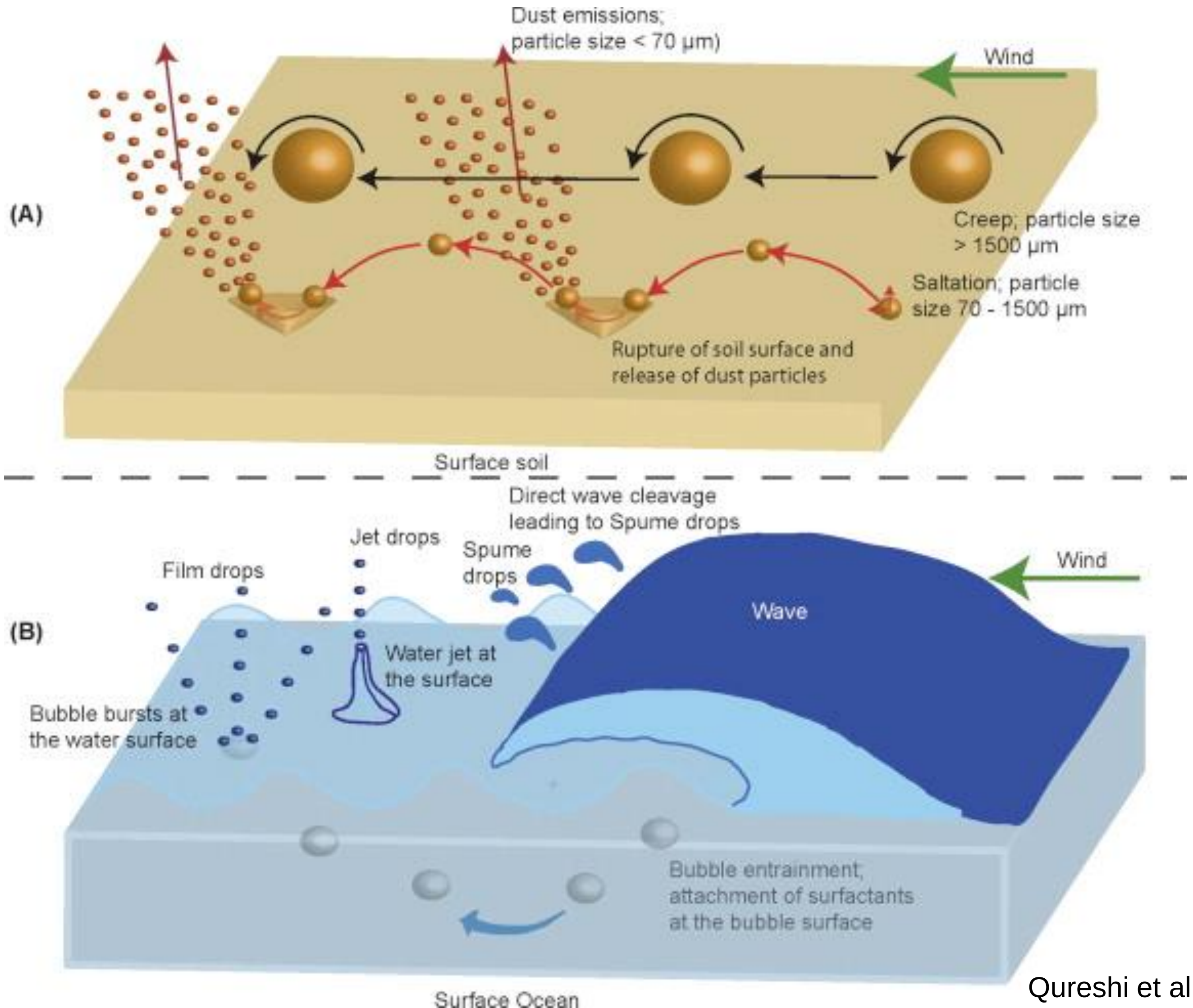


Figure 9. Emission rates of BC in the year 2000 by region, indicating major source categories in each region. SPEW, GAINS, and RETRO emission data are the same as in Figure 8. Regions are shown in Figure 7.

Cookstove in use/*Cheryl Weyant*, http://cee.illinois.edu

earthobservatory.nasa.gov

Suspension of particles from soil and ocean surfaces



Qureshi et al., *Chemosphere*, 2002

Dust resuspension

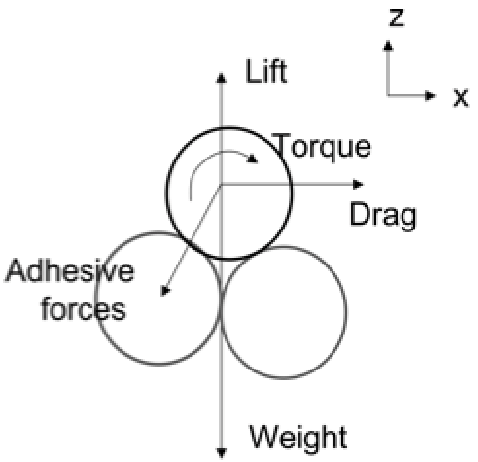
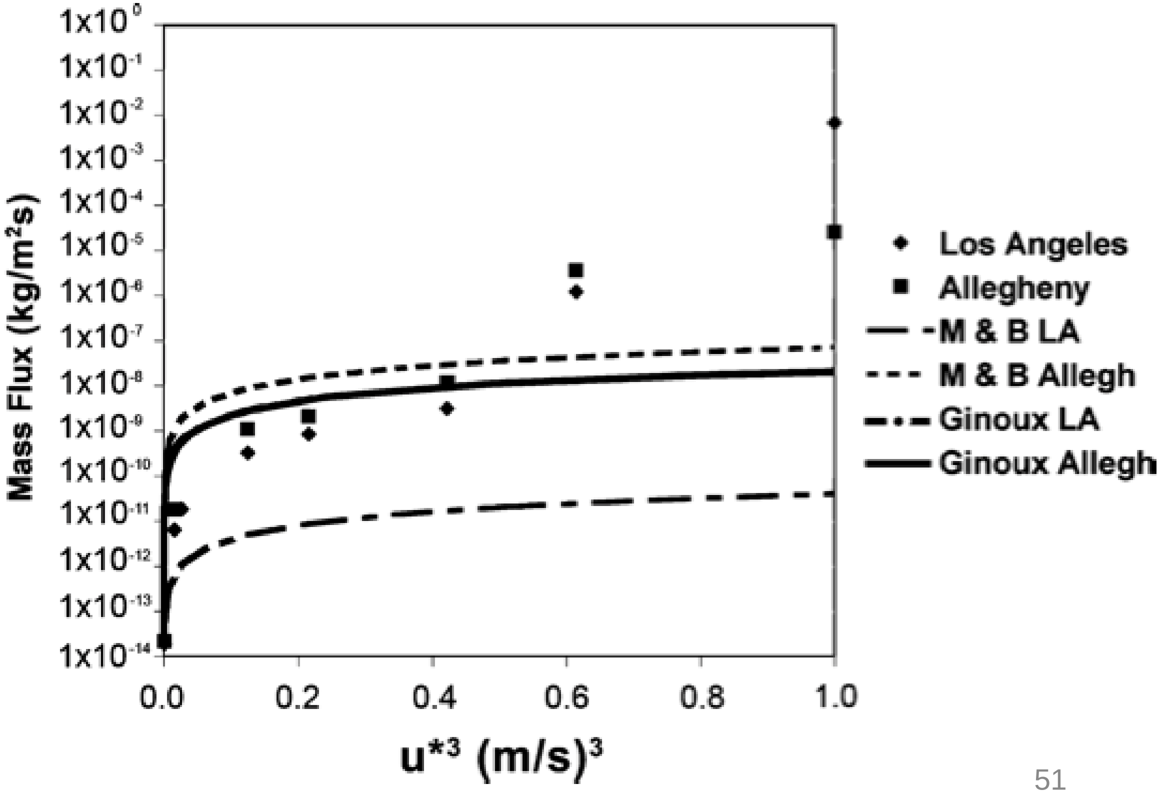


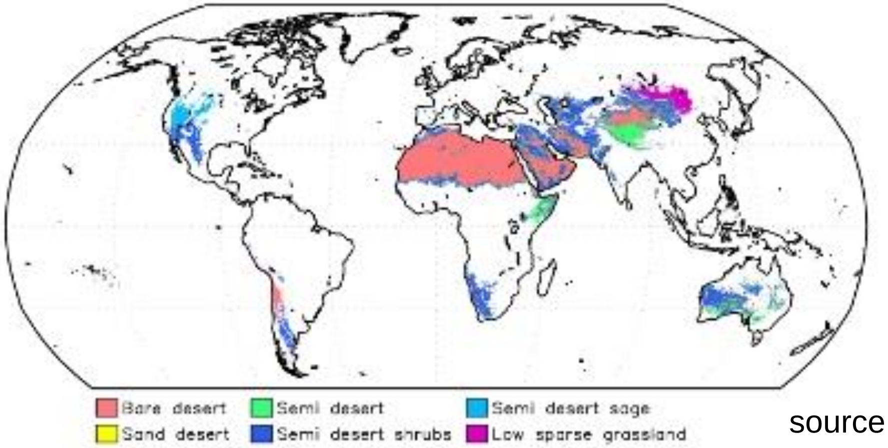
FIG. 1. Force balance acting on a single soil particle subject to aerodynamic and adhesive forces (adapted from Greeley and Iversen, 1985).

Force balance on soil particles (“grains”)

Emissions are dependent on wind speed



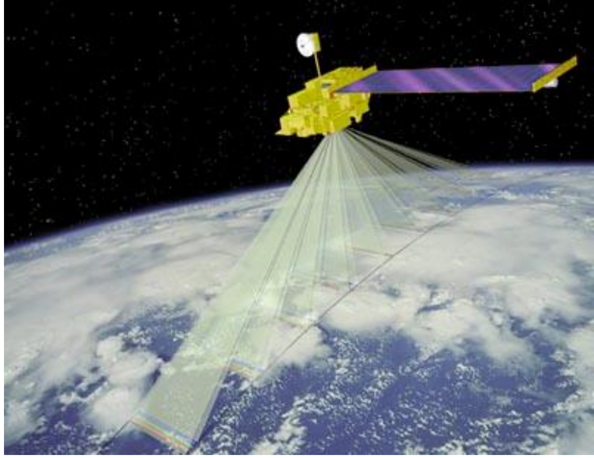
Harris and Davidson, 2009

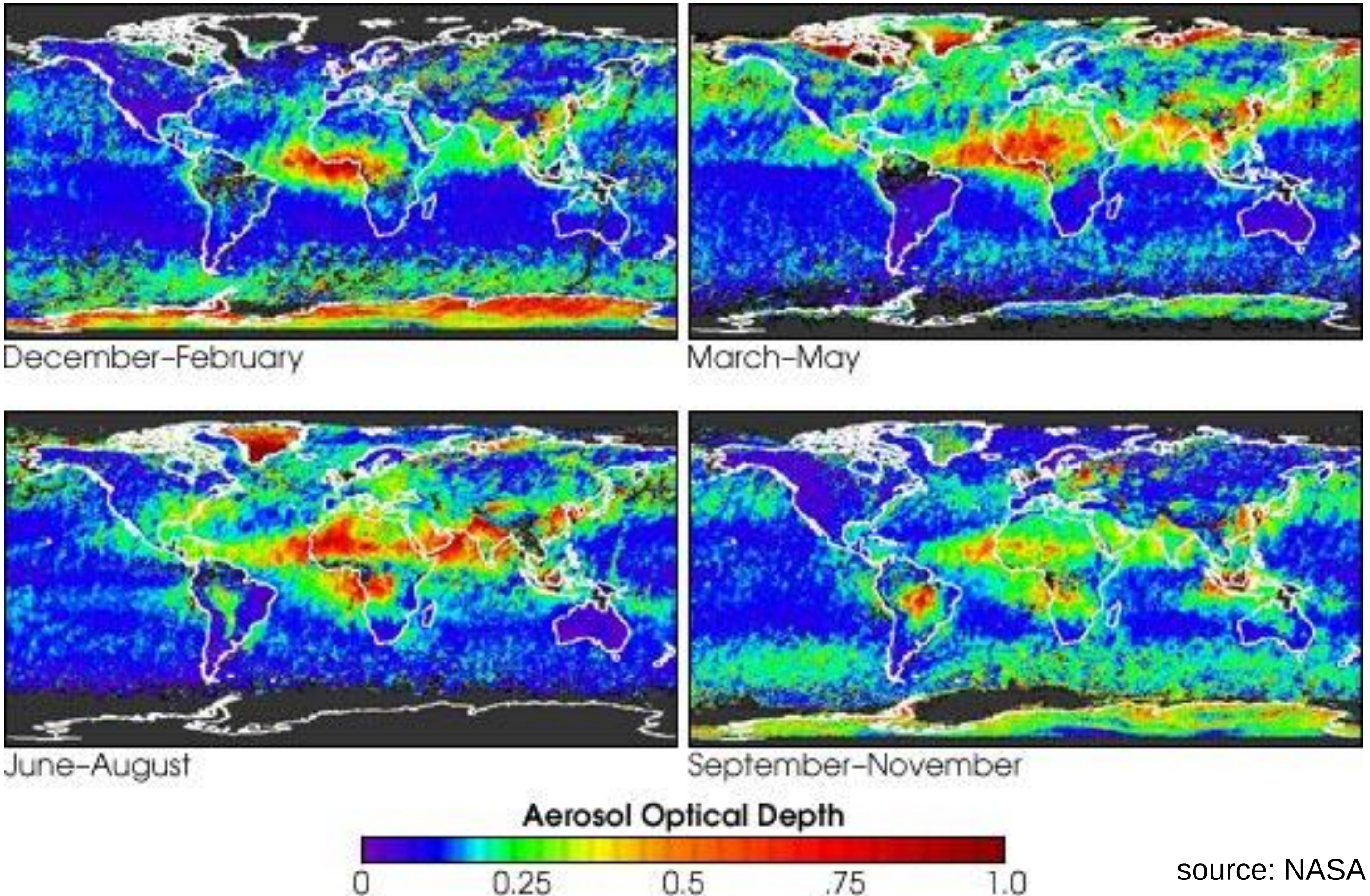


Desert locations

source: WMO

MISR satellite
source: NASA




December-February
March-May
June-August
September-November

Aerosol Optical Depth ~
Column aerosol burden

source: NASA

Sea spray

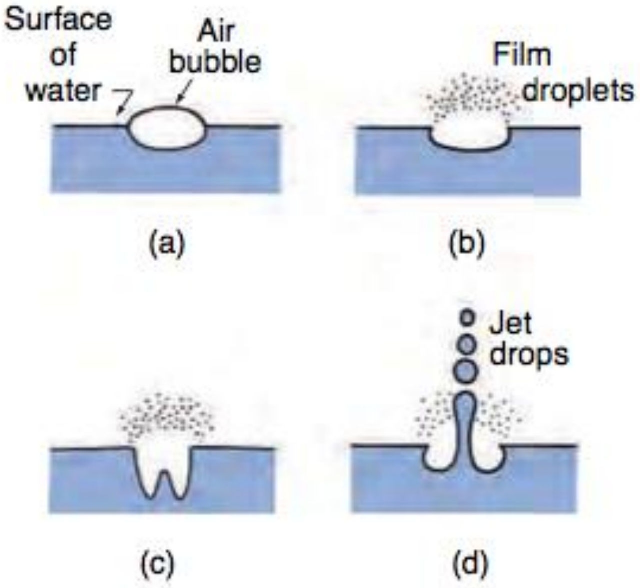
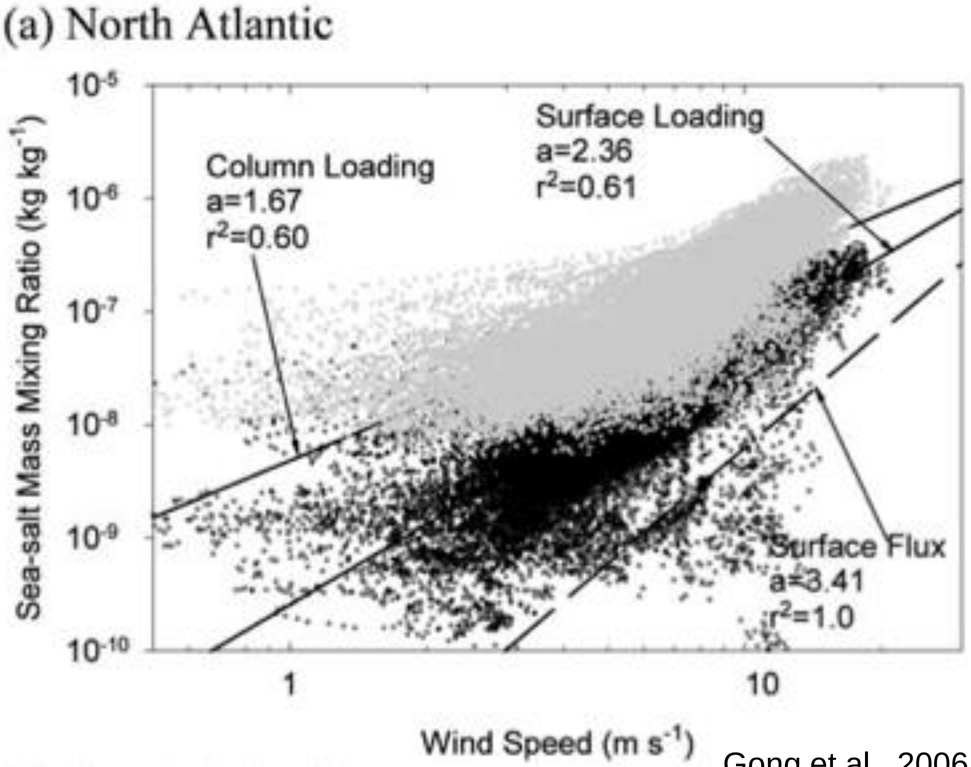


Fig. 5.8 Schematics to illustrate the manner in which film droplets and jet drops are produced when an air bubble bursts at the surface of water. Over the oceans some of the droplets and drops evaporate to leave sea-salt particles and other materials in the air. The time between (a) and (d) is ~2 ms. The film droplets are ~5–30 μm diameter before evaporation. The size of the jet drops are ~15% of the diameter of the air bubble.

Wallace and Hobbs, 2006



Gong et al., 2006

- Entrained air bubbles bursting during whitecap formations due to surface winds.
- A continuous supply of excessive energy by the wind to the sea surface results in wave breaking and consequently whitecaps.
- The production of sea-salt aerosols by wind is proportional to the whitecap coverage.

Agriculture

grazing on pasture

source: Wikipedia

feedlots

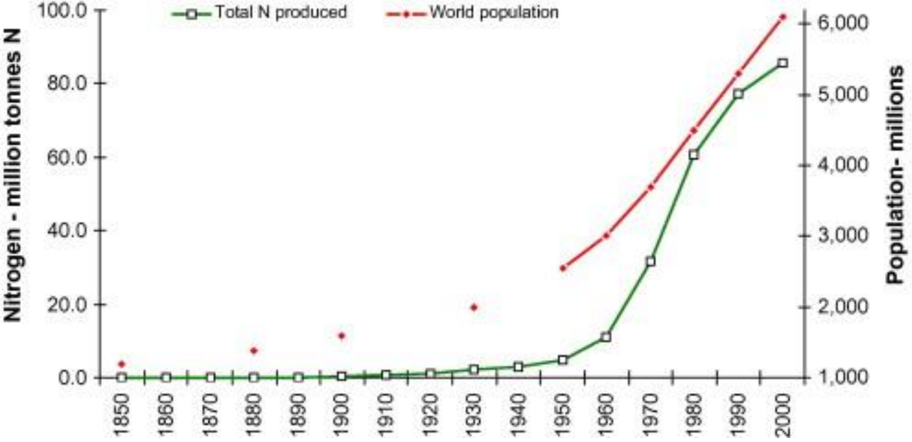
source: The Guardian

fertilizer spreading

source: Deere.com

Major emissions:

- NH_3 (PM precursor),
- N_2O (greenhouse gas)

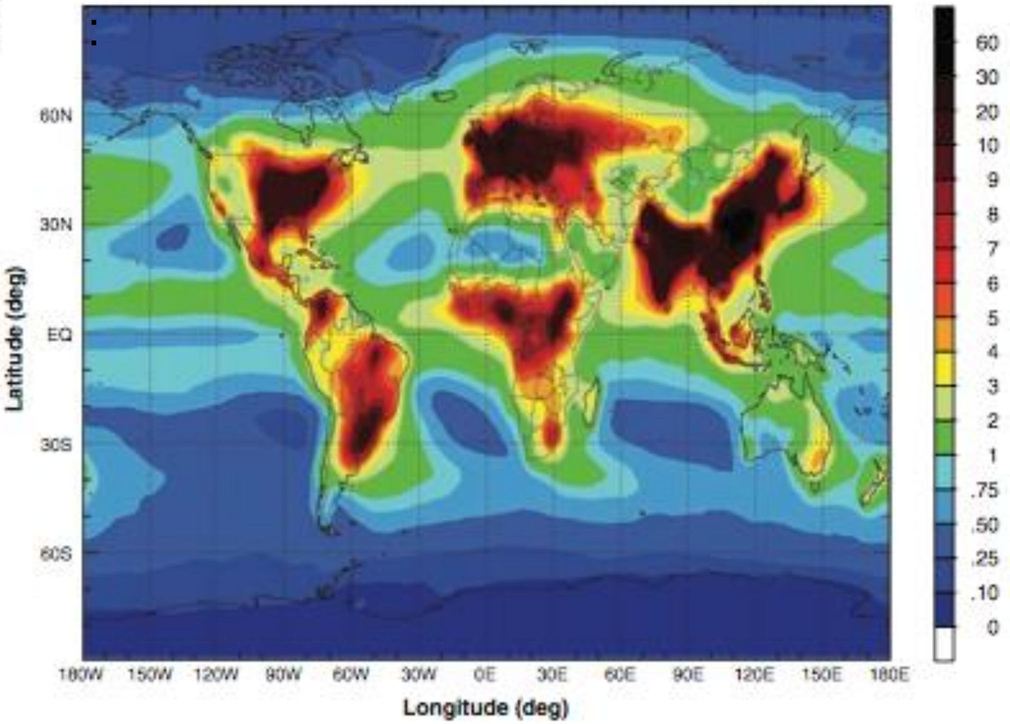


Dawson and Hilton, *Food Policy*, 2011

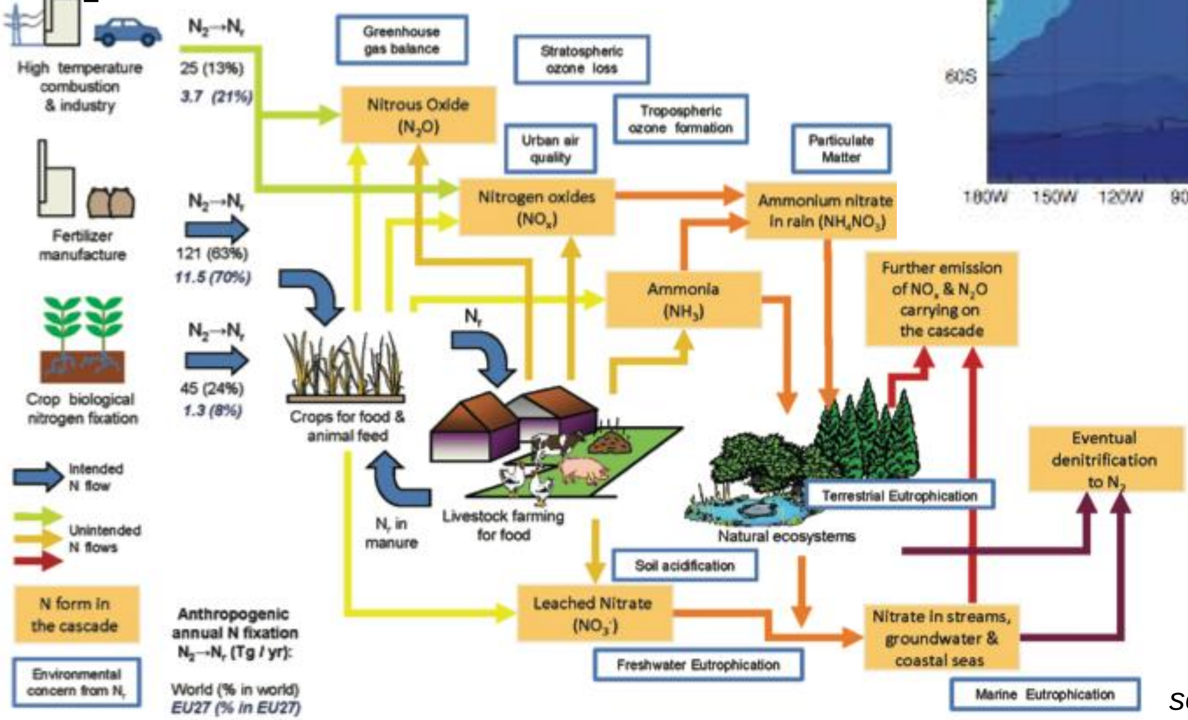
Nitrogen fixation: $N_2 + 3\ H_2 \rightarrow 2\ NH_3$

Emission as NH_3, N_2O:

Deposition (primarily as NH_3 or NH_4NO_3)

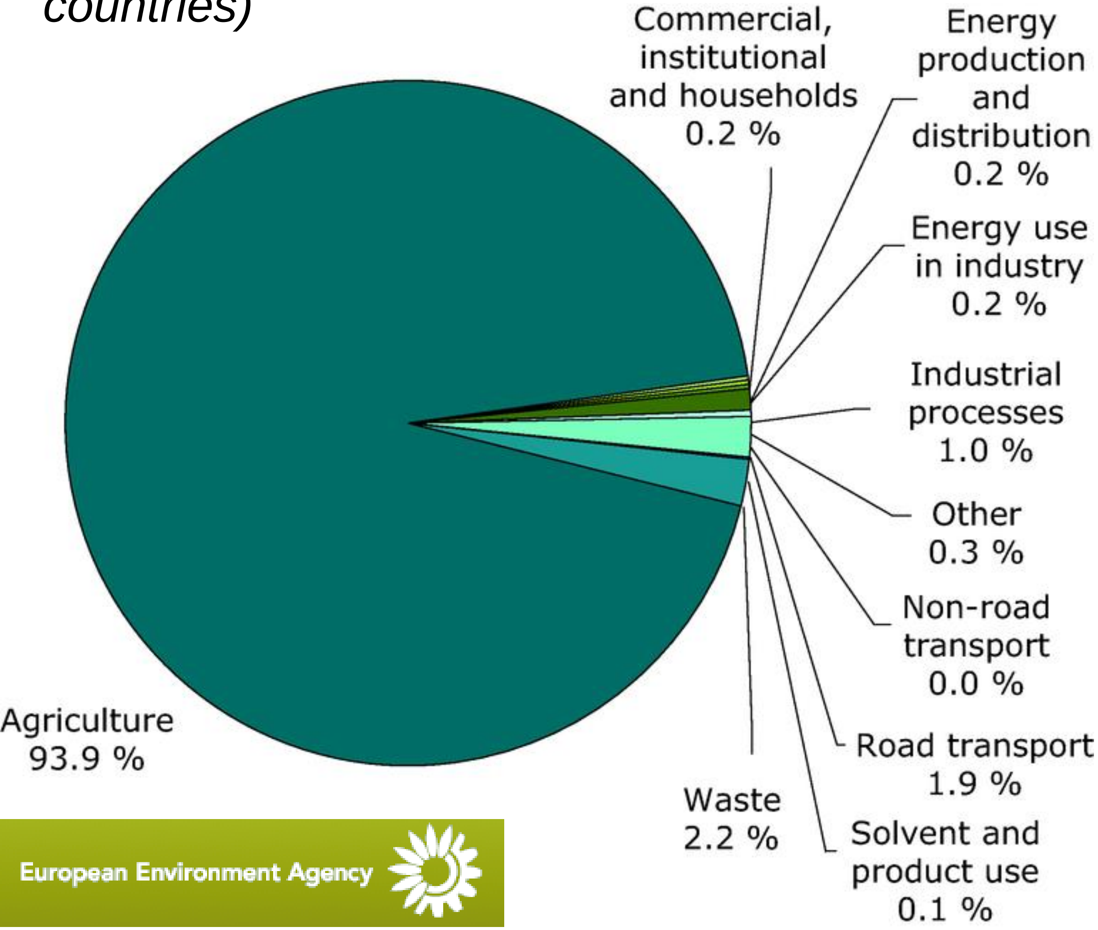


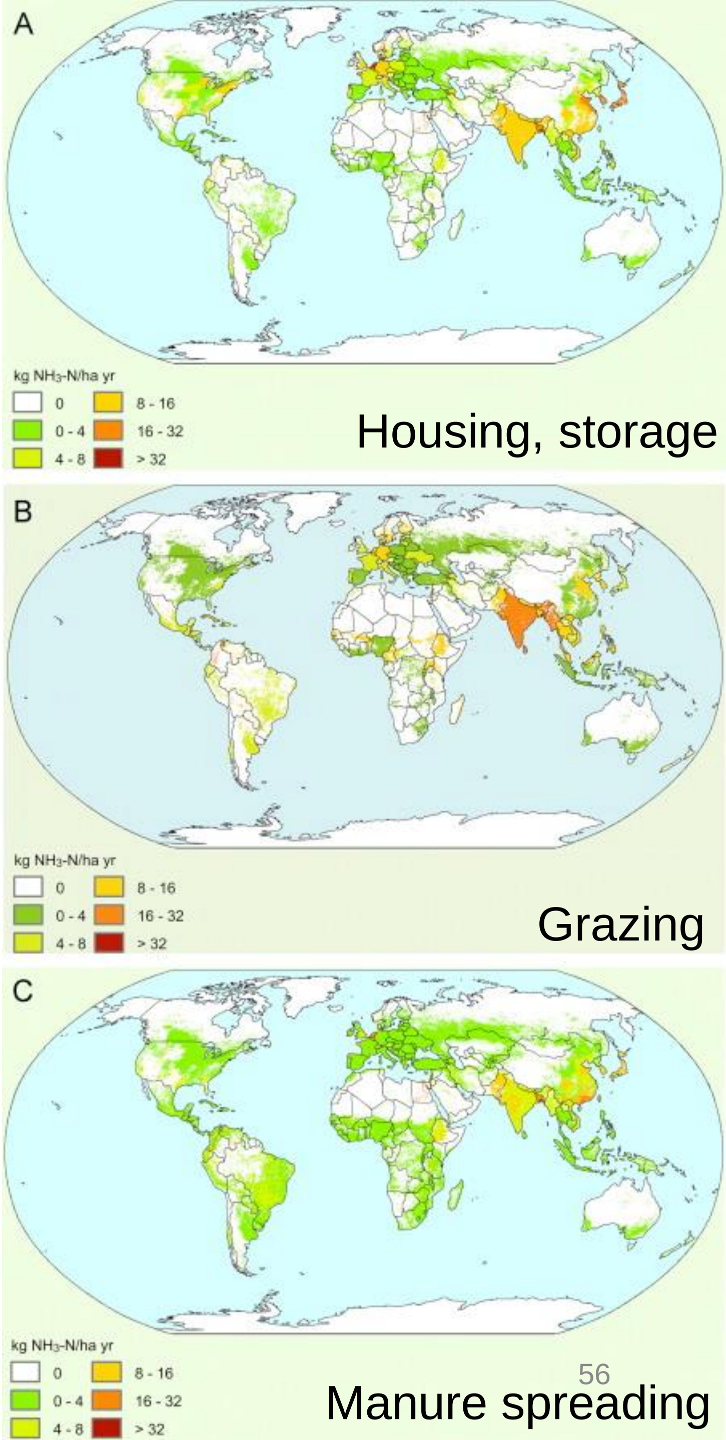
Galloway et al., *Science*, 2008



source: European Nitrogen Assessment, 2011

Sector share of ammonia emissions (EEA member countries)





Beusen et al., *Atmos. Environ.*, 2008

ESTIMATION METHODS

Given the complexity of the physical/chemical processes leading to many types of emissions, measurements are often used to estimate emission factors in these cases.

Approaches to solve the inverse problem of estimating emissions based on emissions coupled to a physical/chemical model also exist.

Industrial emissions:

- Stack monitoring

Vehicle emissions:

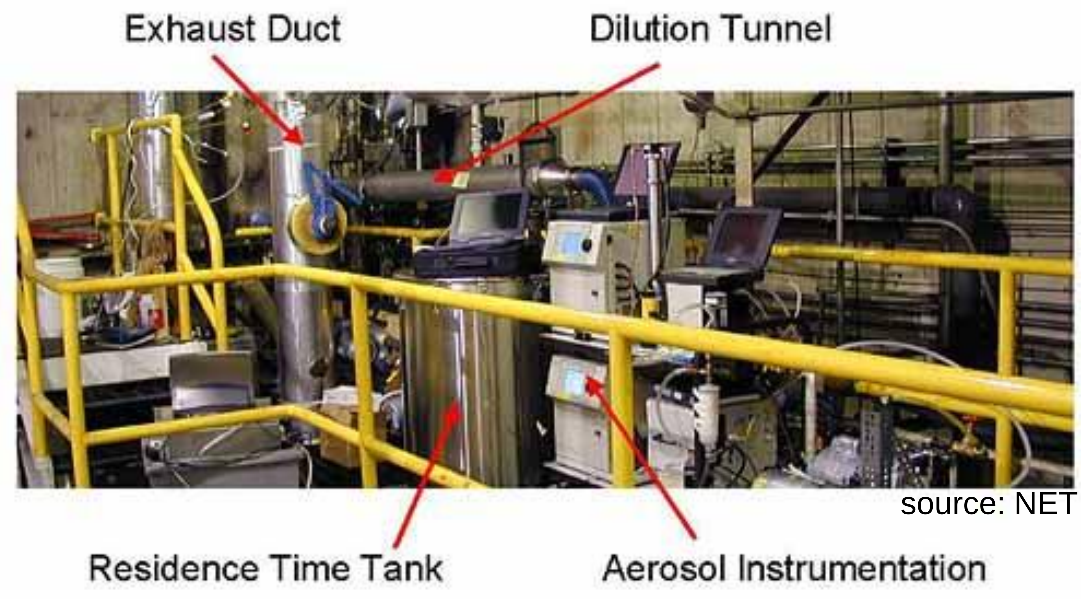
- Dynamometer
- Tunnel studies
- Chamber

Biogenic emissions:

- Chamber
- Flux tower

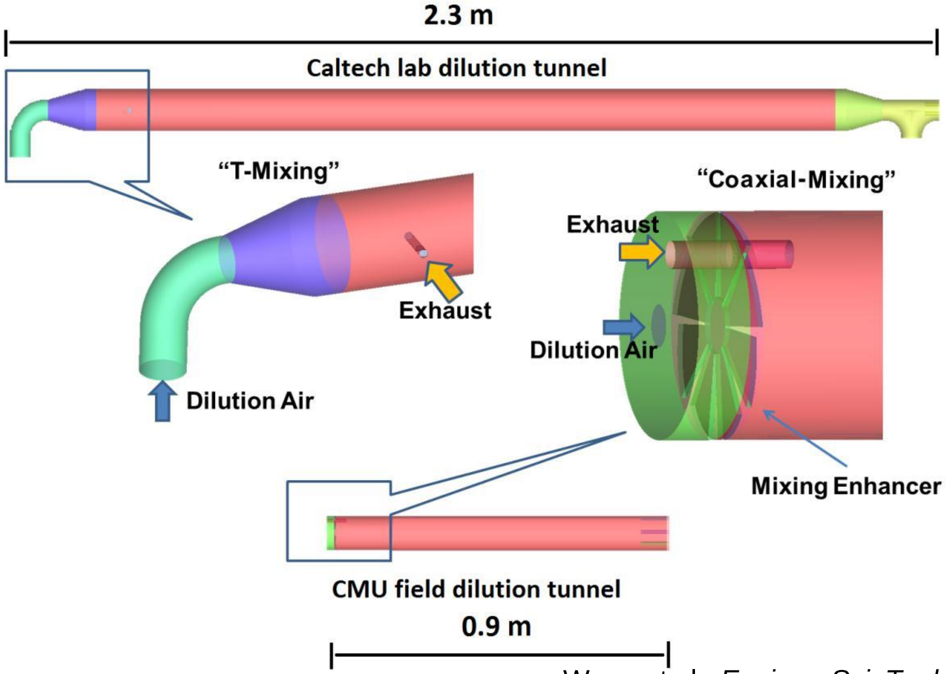
Dynamometer

Maricq, 2007

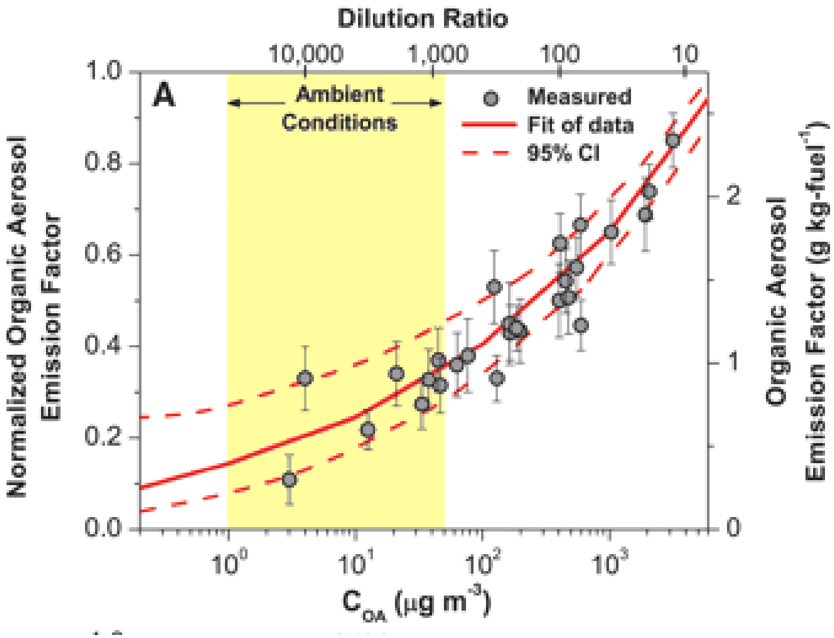


source: NETL

Many types of hot emissions are diluted to simulate ambient conditions (lower temperatures)



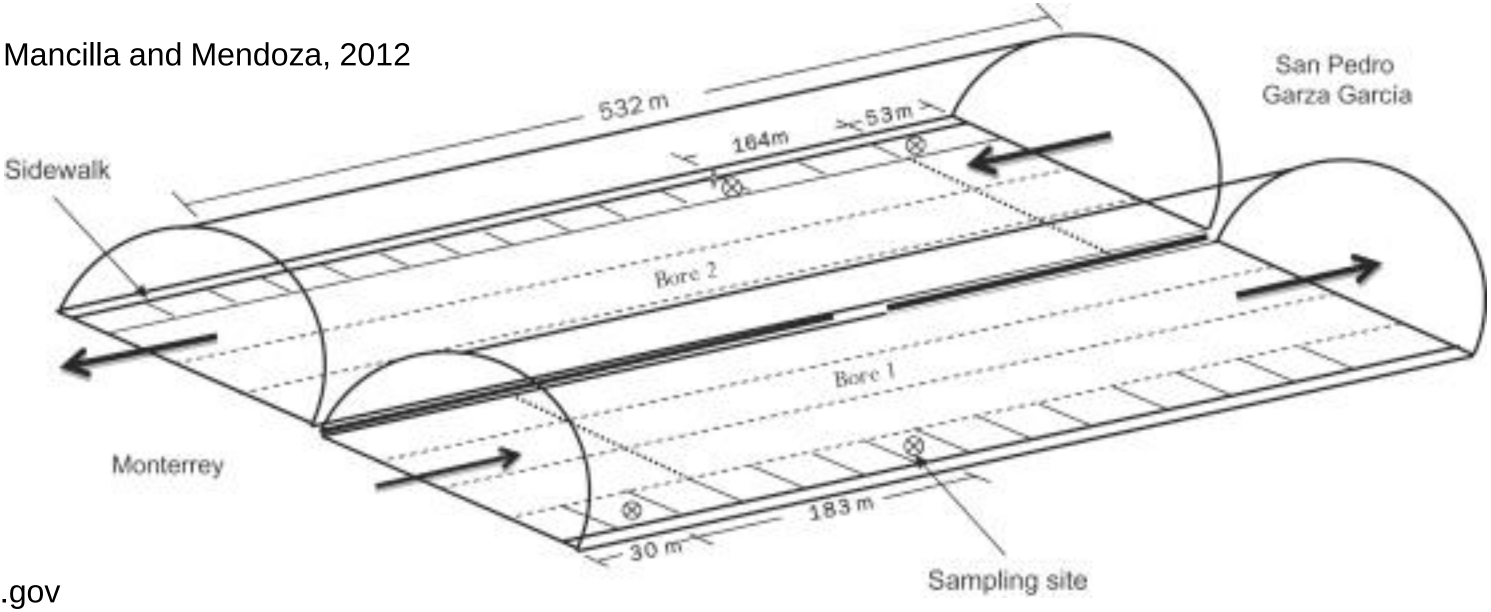
Wang et al., *Environ. Sci. Tech.*, 2013



Robinson et al., *Science*, 2007

Tunnel study

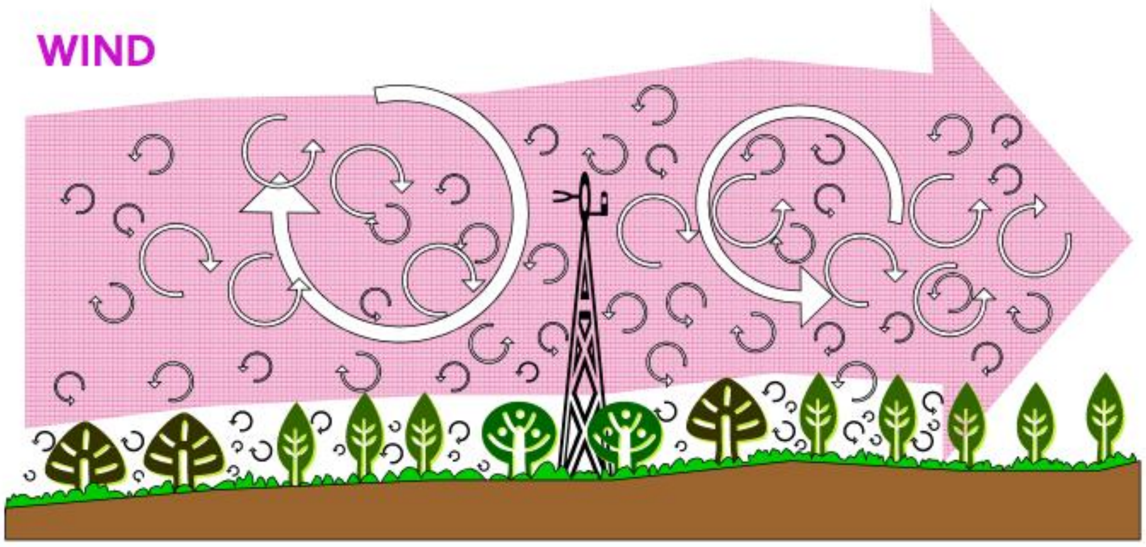
Mancilla and Mendoza, 2012



www.mtc.ca.gov

- Measure emissions in tunnel
- Count number of vehicles entering (classify according to vehicle class: light-duty, heavy-duty, passenger vehicle, truck, etc.)
- Overall emission factor

Measuring area fluxes over different land types by eddy covariance



- Air flow can be imagined as a horizontal flow of numerous rotating eddies
- Each eddy has 3-D components, including a vertical wind component
- The diagram looks chaotic but components can be measured from tower

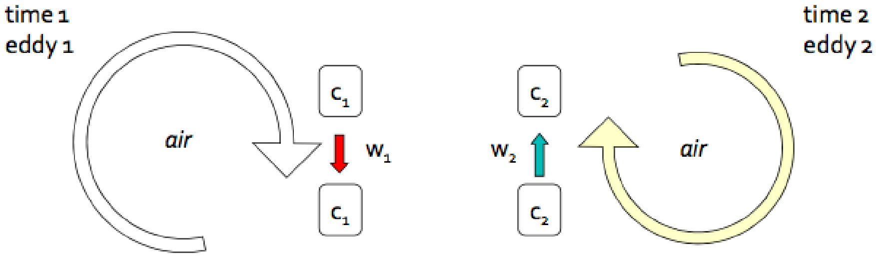
Burba et al., 2011

Fluxes for species j are calculated from time-averaged product of vertical wind velocities and concentrations deviating from their mean values over a fixed time interval $k = \{1, 2, \ldots, N\}$:

$$F_j = \overline{w'\chi_j'} = \frac{1}{N}\sum_{k=1}^{N} w'(t_k)\,\chi_j'(t_k)$$

- F_j = flux (mass per time)
- w' = instantaneous deviation of vertical wind velocity (length per time)
- χ_j' = instantaneous deviation of mass concentration (mass per volume)

www.geos.ed.ac.uk



At a single point on the tower:

Eddy 1 moves parcel of air c_1 down with the speed w_1 then Eddy 2 moves parcel c_2 up with the speed w_2

Each parcel has concentration, temperature, humidity; if we know these and the speed – we know the flux

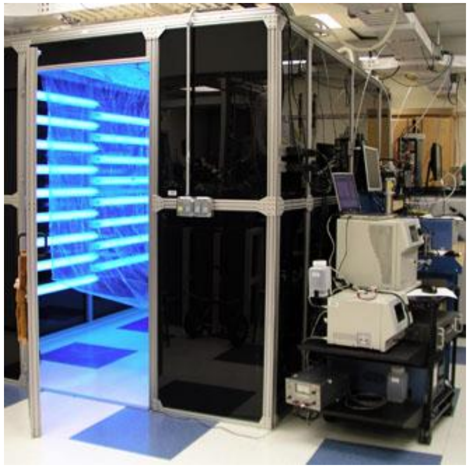
Emission factors and reactivity from chamber studies

- Investigate emissions from plants, patch of land, and other things
- Create your own atmosphere
- Investigate chemical reactions – production of O_3 and PM
  - inject VOCs, oxidants
  - subject to UV or sunlight

UNC Chapell Hill

Jülich

UNC Chapell Hill



UC Irvine

UC Boulder

Controlled burning studies

source: http://lamar.colostate.edu/

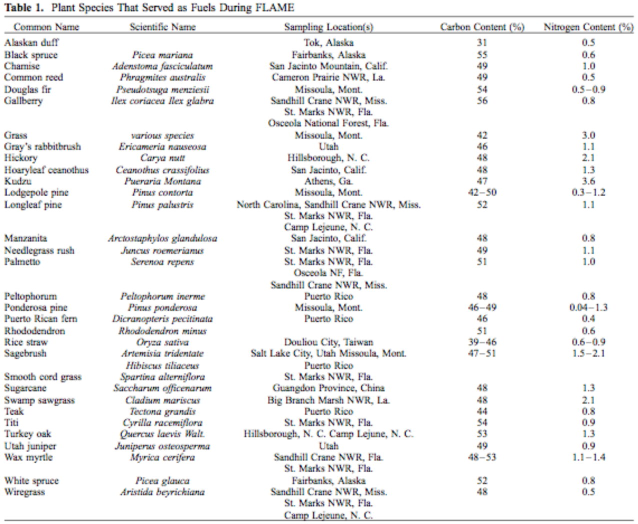


Table 1. Plant Species That Served as Fuels During FLAME

Common Name	Scientific Name	Sampling Location(s)	Carbon Content (%)	Nitrogen Content (%)
Alaskan duff		Tok, Alaska	31	0.5
Black spruce	*Picea mariana*	Fairbanks, Alaska	55	0.6
Chamise	*Adenstoma fasciculatum*	San Jacinto Mountain, Calif.	49	1.0
Common reed	*Phragmites australis*	Cameron Prairie NWR, La.	49	0.5
Douglas fir	*Pseudotsuga menziesii*	Missoula, Mont.	54	0.5–0.9
Gallberry	*Ilex coriacea Ilex glabra*	Sandhill Crane NWR, Miss. St. Marks NWR, Fla. Osceola National Forest, Fla.	56	0.8
Grass	*various species*	Missoula, Mont.	42	3.0
Gray's rabbitbrush	*Ericameria nauseosa*	Utah	46	1.1
Hickory	*Carya nutt*	Hillsborough, N. C.	48	2.1
Hoaryleaf ceanothus	*Ceanothus crassifolius*	San Jacinto, Calif.	48	1.3
Kudzu	*Pueraria Montana*	Athens, Ga.	47	3.6
Lodgepole pine	*Pinus contorta*	Missoula, Mont.	42–50	0.3–1.2
Longleaf pine	*Pinus palustris*	North Carolina, Sandhill Crane NWR, Miss. St. Marks NWR, Fla. Camp Lejeune, N. C.	52	1.1
Manzanita	*Arctostaphylos glandulosa*	San Jacinto, Calif.	48	0.8
Needlegrass rush	*Juncus roemerianus*	St. Marks NWR, Fla.	49	1.1
Palmetto	*Serenoa repens*	St. Marks NWR, Fla. Osceola NF, Fla. Sandhill Crane NWR, Miss.	51	1.0
Peltophorum	*Peltophorum inerme*	Puerto Rico	48	0.8
Ponderosa pine	*Pinus ponderosa*	Missoula, Mont.	46–49	0.04–1.3
Puerto Rican fern	*Dicranopteris pecitinata*	Puerto Rico	46	0.4
Rhododendron	*Rhododendron minus*		51	0.6
Rice straw	*Oryza sativa*	Douliou City, Taiwan	39–46	0.6–0.9
Sagebrush	*Artemisia tridentate*	Salt Lake City, Utah Missoula, Mont.	47–51	1.5–2.1
	Hibiscus tiliaceus	Puerto Rico		
Smooth cord grass	*Spartina alterniflora*	St. Marks NWR, Fla.		
Sugarcane	*Saccharum officenarum*	Guangdon Province, China	48	1.3
Swamp sawgrass	*Cladium mariscus*	Big Branch Marsh NWR, La.	48	2.1
Teak	*Tectona grandis*	Puerto Rico	44	0.8
Titi	*Cyrilla racemiflora*	St. Marks NWR, Fla.	54	0.9
Turkey oak	*Quercus laevis Walt.*	Hillsborough, N. C. Camp Lejune, N. C.	53	1.3
Utah juniper	*Juniperus osteosperma*	Utah	49	0.9
Wax myrtle	*Myrica cerifera*	Sandhill Crane NWR, Fla. St. Marks NWR, Fla.	48–53	1.1–1.4
White spruce	*Picea glauca*	Fairbanks, Alaska	52	0.8
Wiregrass	*Aristida beyrichiana*	Sandhill Crane NWR, Miss. St. Marks NWR, Fla. Camp Lejeune, N. C.	48	0.5

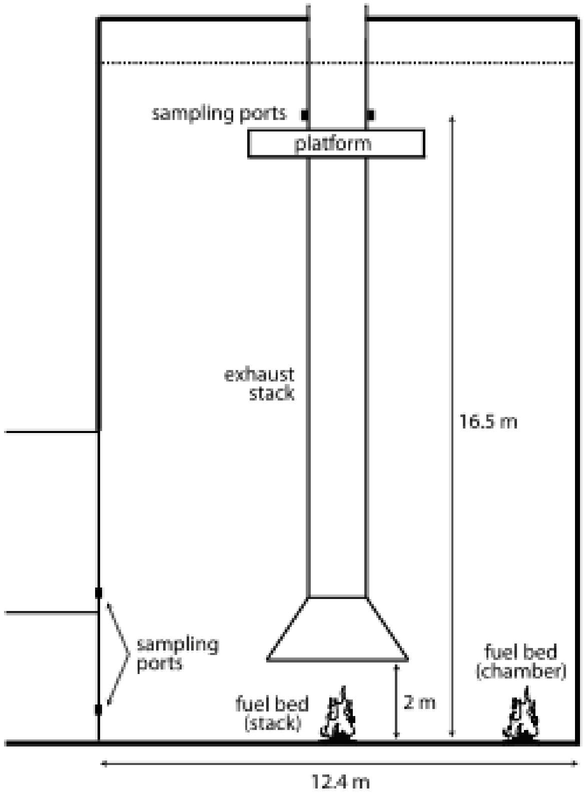
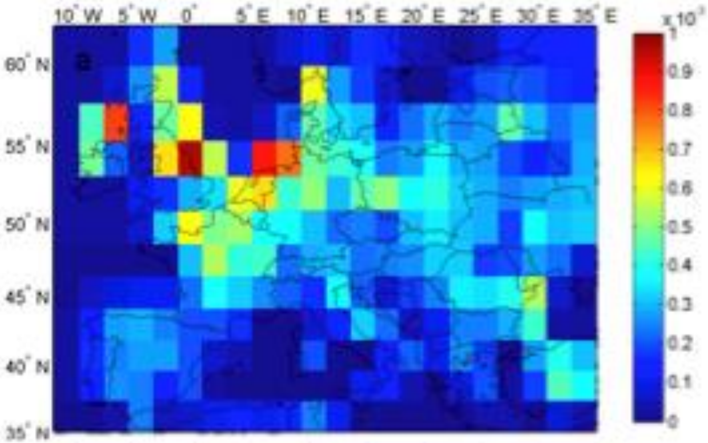


Figure 1. Schematic of the U.S. Forest Service Fire Sciences Laboratory combustion facility, located in Missoula, Montana. Image is to scale. The locations of the fuel bed and of the sampling ports during stack and chamber burns are indicated.

McMeeking et al., *J. Geophys. Res.*, 2009

Inverse modeling

N_2O fluxes over Europe



Thompson et al., *Atmos. Chem. Phys.*, 2011

Given model F and its parameters p, observations of variables y (with initial and boundary conditions) as a function of position $\mathbf{r}$ and time t, find emissions E:

$$y(\mathbf{r}, t) = F(y_0(\mathbf{r}), y_{\mathbf{r}}(t), E, p)$$

Observations may be from in-situ or remote sensing measurements

NH_3 emissions over U.S.

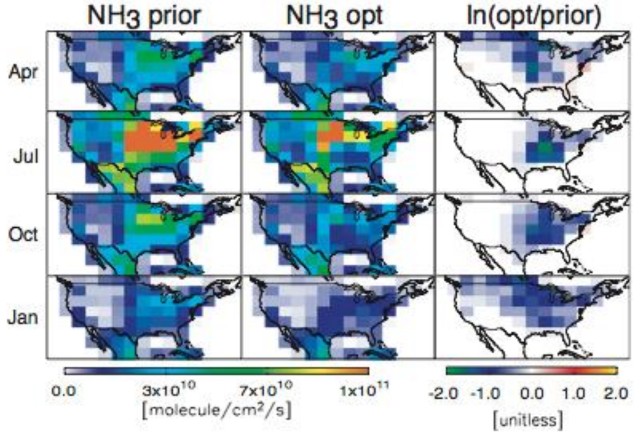


Fig. 8. Anthropogenic NH_3 emissions. The left column shows the prior inventory, the center the optimized inventory, and the right column the logarithmic scaling factors (σ).

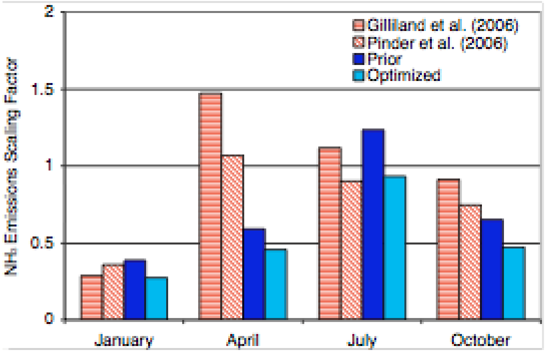


Fig. 10. Monthly emissions scaling factors for US emissions of NH_3 from all sources. Scaling is with respect to the NEI99 monthly value of 3.6 Tg N/yr. The initial GEOS-Chem simulation is shown in dark blue, with the optimized monthly scaling factors comprised of separate scaling factors in each grid cell are in light blue. The red striped bars show the inverse modeling estimates of Gilliland et al. (2006) (horizontal lines) and the process based estimates of Pinder et al. (2006) (diagonal lines). Note the modeling domain and prior emissions inventories for the latter two works are different than that of the present work.

Henze et al, *Atmos. Chem. Phys.*, 2009

CONTROL OF EMISSIONS

Control of primary particulate matter

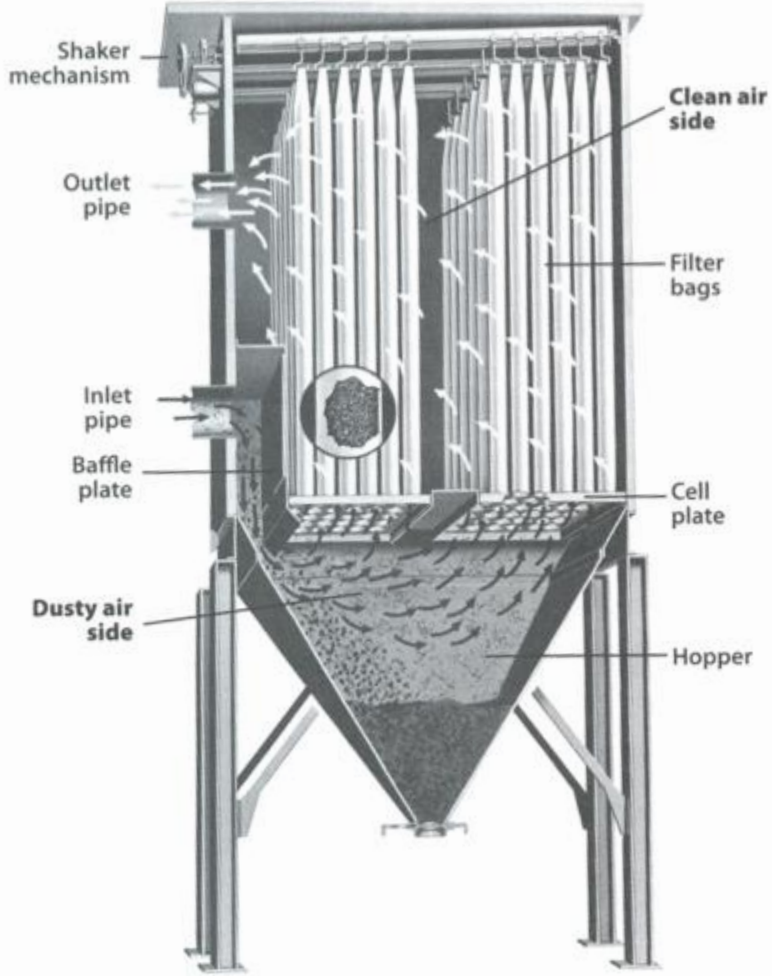


Figure 6.3
Cutaway view of a shaker baghouse.
(Courtesy of Siemens Energy, Inc., Orlando, FL.)

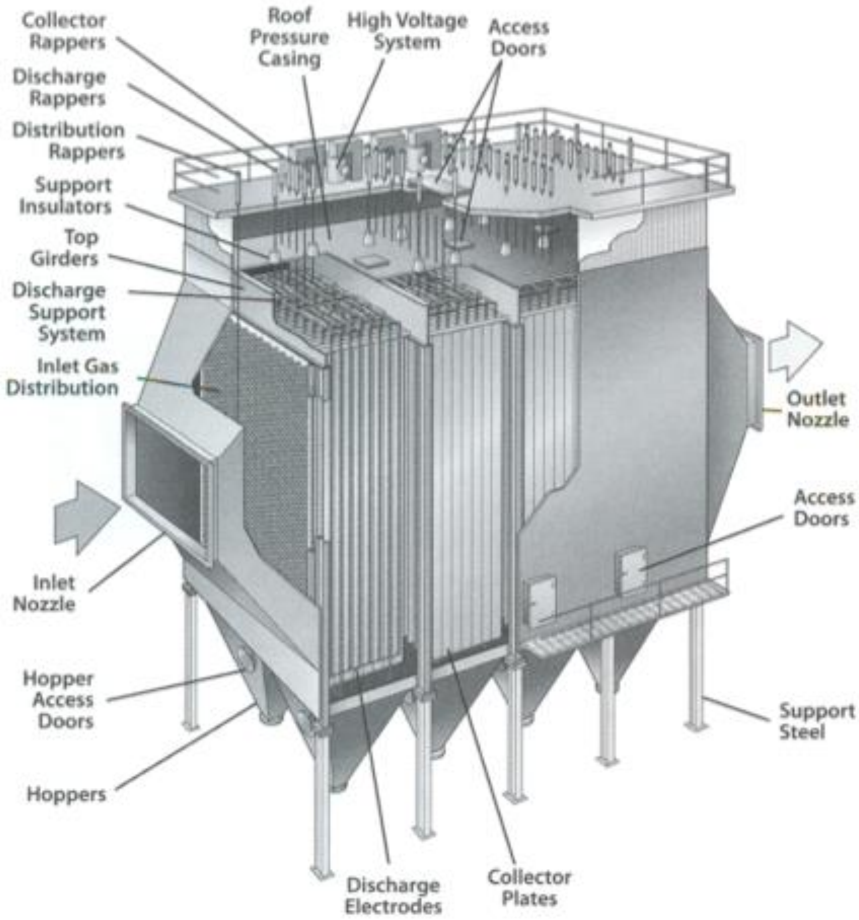


Figure 5.2
Cutaway view of an electrostatic precipitator.
(Courtesy of the Babcock & Wilcox Company, Barberton, OH.)

Control of gases and vapors

- adsorption onto surface of solids
- absorption into liquid solvents
- conversion to another chemical form by oxidation (catalytic or direct flame incineration)
- change original chemical process which produces the pollutant

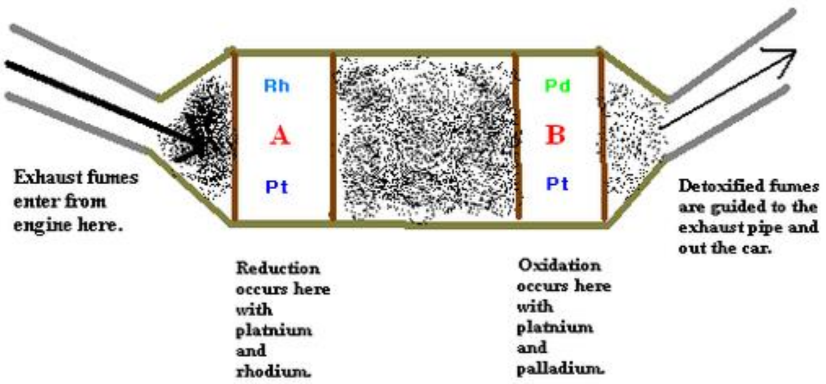
source: newscientist.com

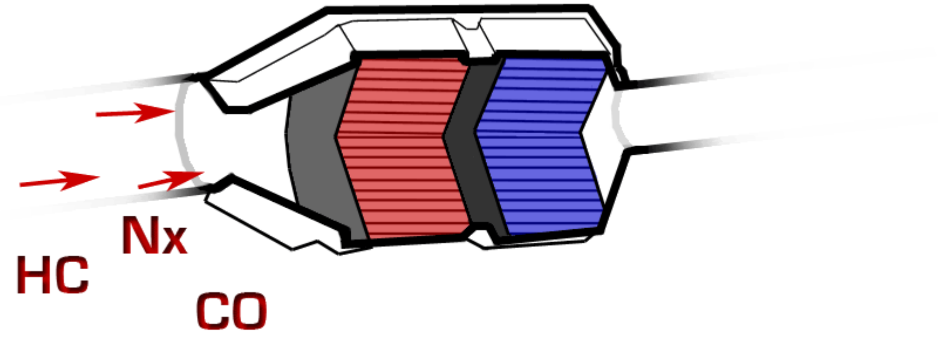
NO_x control

Catalytic converters:

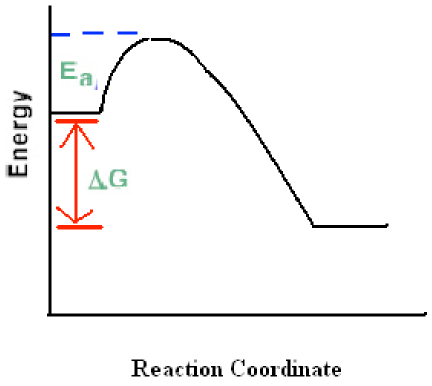
- Reduce NO_x (possible formation of NH_3)
- Also allows oxidation of CO and hydrocarbons at lower temperatures
- Redox reactions on surfaces of platinum, rhodium, and palladium

$$\begin{aligned} NO_x &\rightarrow N_x + O_x \\ CO + O_2 &\rightarrow CO_2 \\ C_xH_{4x} + 2xO_2 &\rightarrow xCO_2 + 2xH_2O \end{aligned}$$

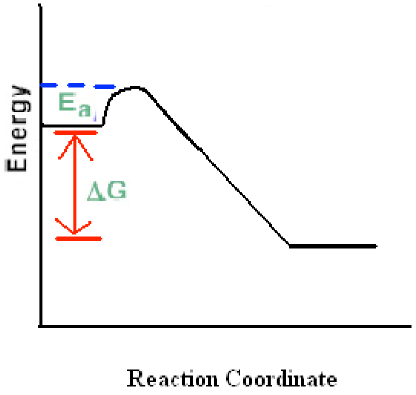




A. Without a catalyst. Note the higher activation energy required for the process to start. Reaction would take longer to form and products would gradually form.



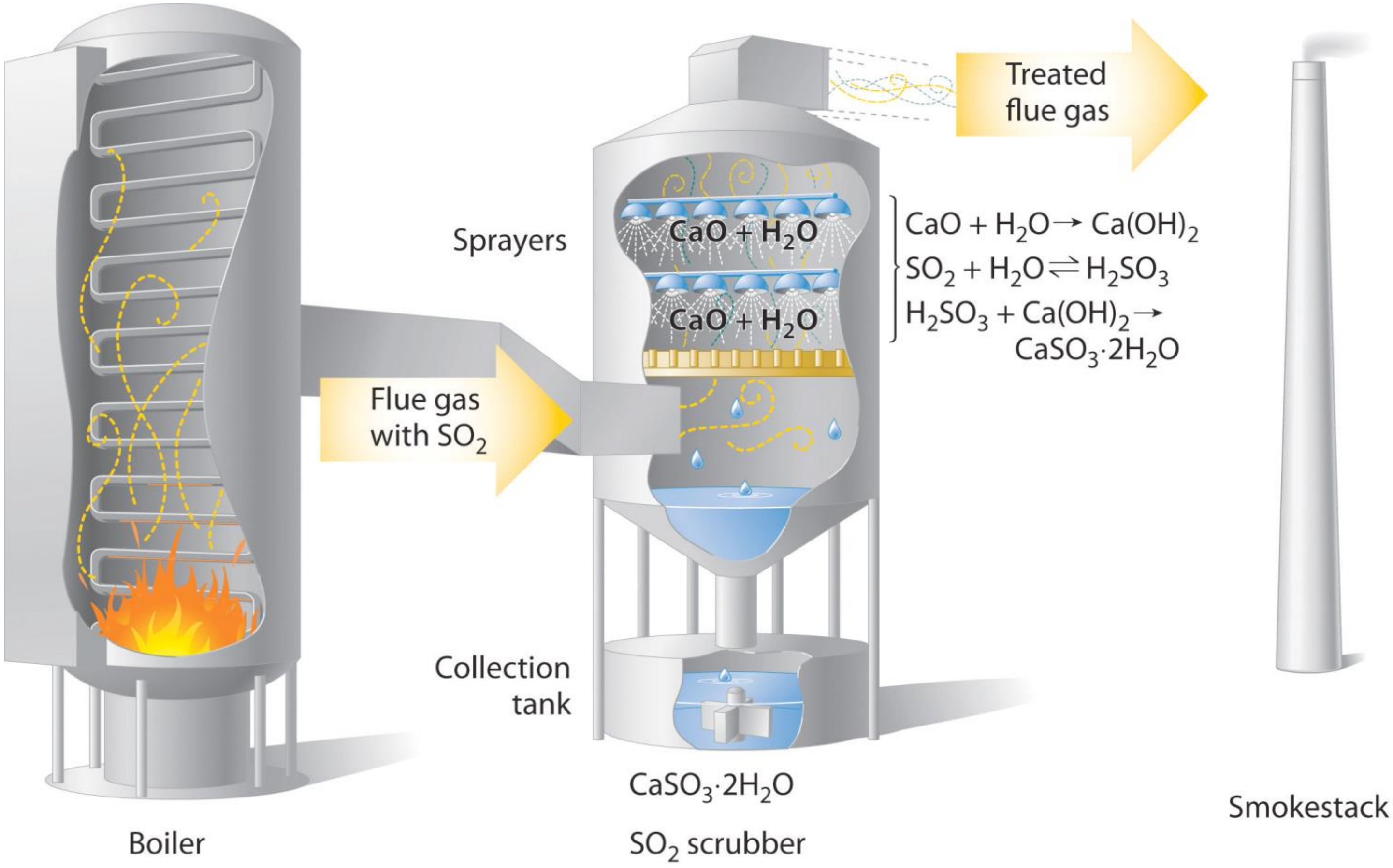
B. With the help of a catalyst, the activation energy required for the reaction goes down significantly. This means the process would go faster and yield more of the products.



source: UCDavis Chemwiki

SO_2 scrubber

trap SO_2 by reaction
with lime (CaO)



source: UCDavis Chemwiki

Figure 1.14 ▷ Typical emissions control systems for power plants

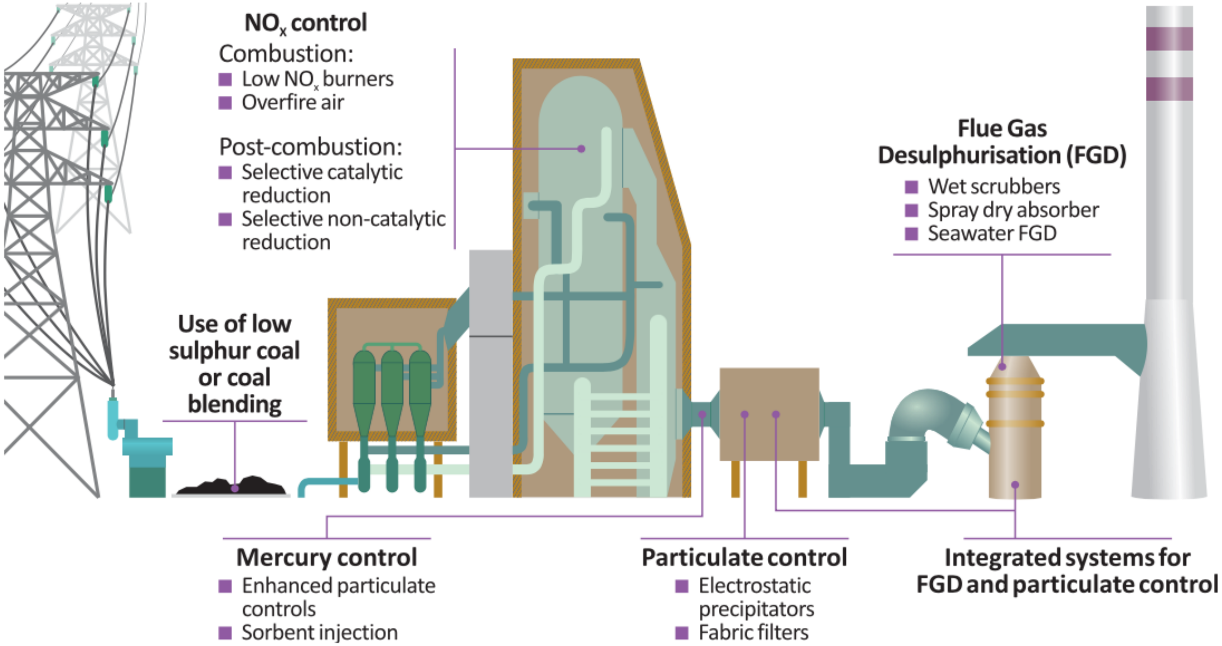


Table 1.4 ▷ Selected mitigation technologies for air pollutants in power generation and industry

Pollutant	Mitigation technology	Type of technology	Abatement efficiency
SO$_2$	Wet flue-gas desulfurisation	End-of-pipe	70-98%*
	Spray-drier absorption	End-of-pipe	50-70%
NO$_X$	Low and ultralow-NO$_X$ burners	Integral to combustion process	20-30%
	Selective catalytic reduction	End-of-pipe	90%
	Selective non-catalytic reduction	End-of-pipe	<50%
PM$_{2.5}$	Fabric filtration	End-of-pipe	>99%
	Electrostatic precipitators	End-of-pipe	>99%

*Abatement efficiency based on coals with 0.3-4.8% sulfur content.

Sources: Nalbandian-Sudgen, H.; IEA Clean Coal Centre (2006) and IEA analysis.

Carbon capture and storage (CCS)

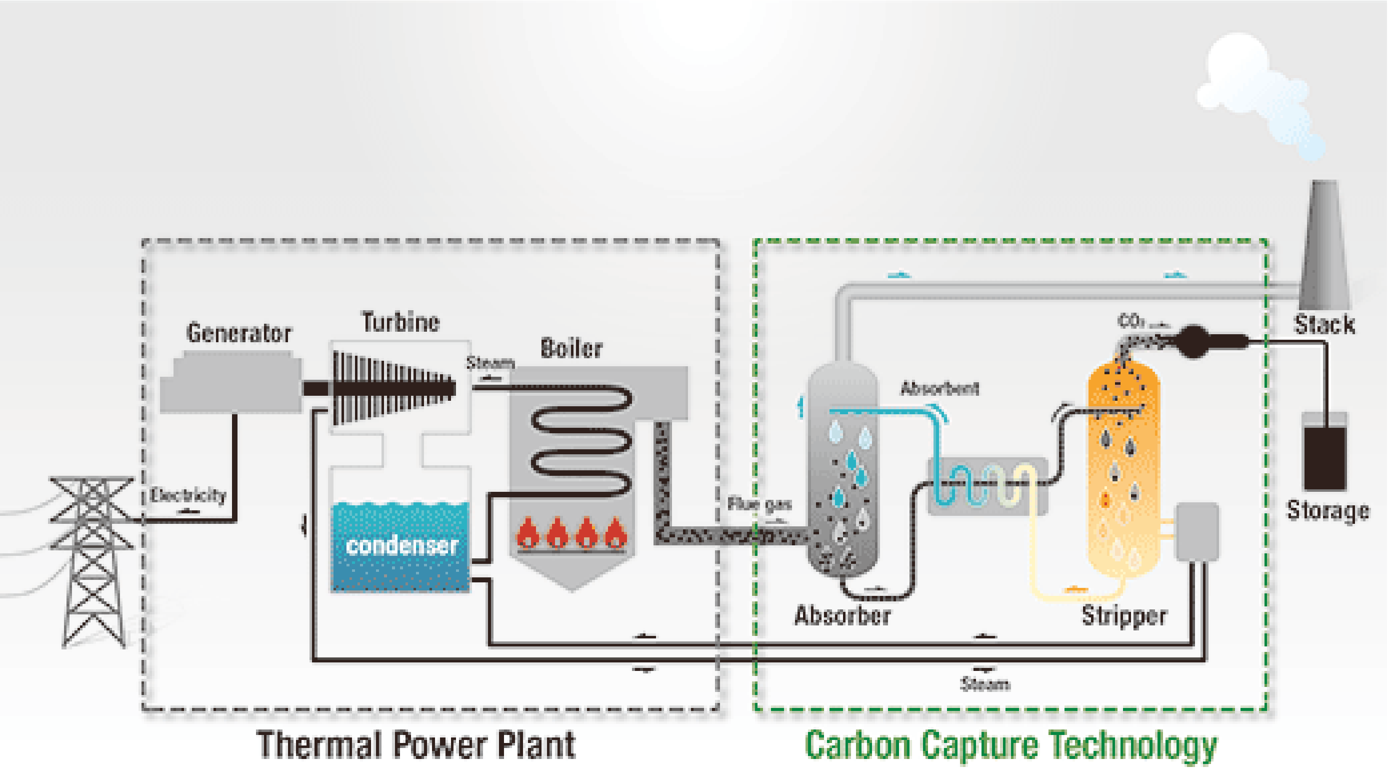
Amines (-NH_2) are weak bases in solution and can neutralize weak acids ($CO_{2(aq)}$).

$$R^1R^2NH + CO_2 + B \rightleftarrows R^1R^2NCOO^- + BH^+$$

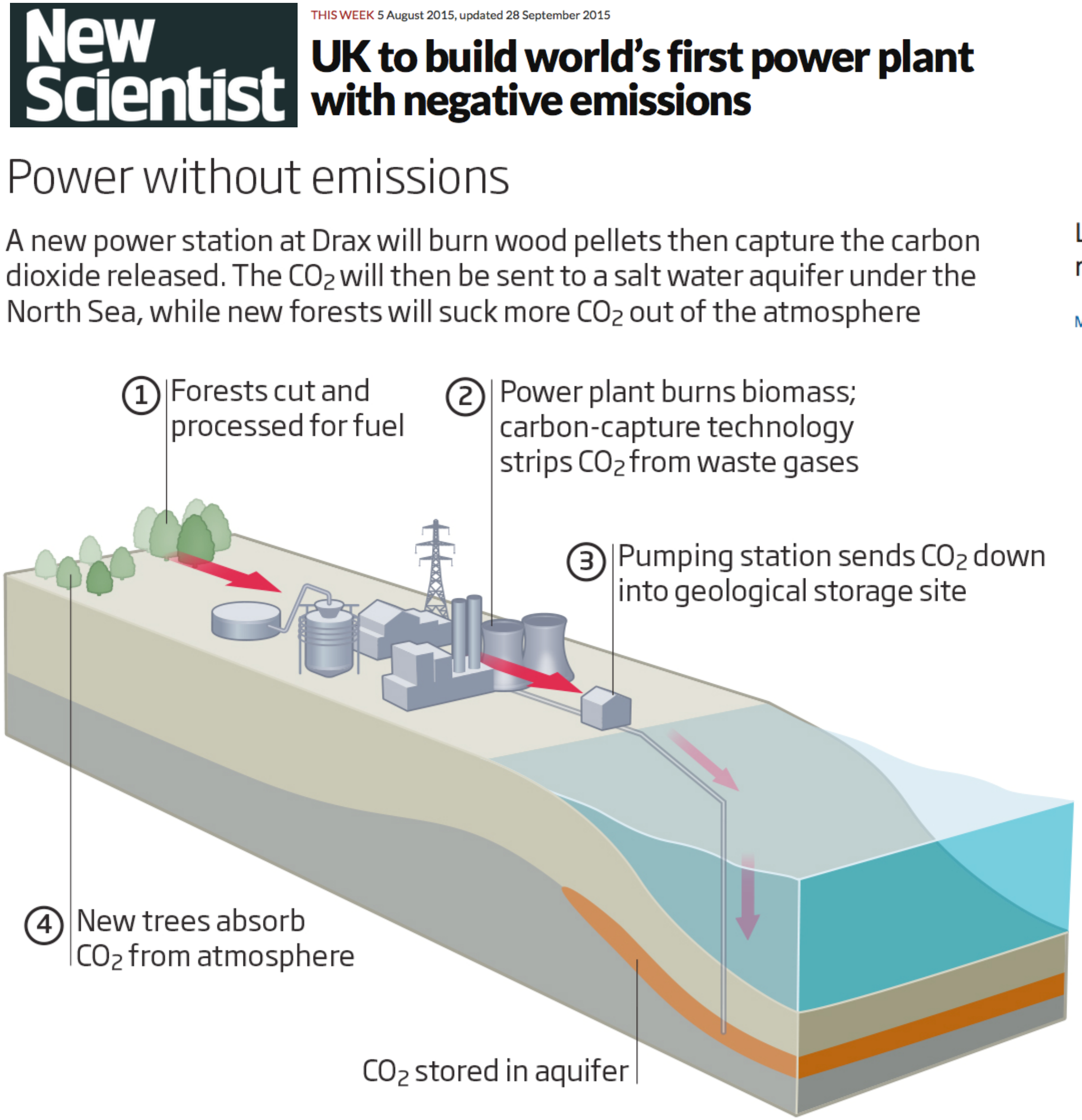
carbamide anion

$$R^1R^2R^3N + CO_2 + H_2O \rightleftarrows HCO_3^- + R^1R^2R^3NH^+$$

bicarbonate anion



source: www.toshiba.co.jp



New Scientist

THIS WEEK 5 August 2015, updated 28 September 2015

UK to build world's first power plant with negative emissions

Power without emissions

A new power station at Drax will burn wood pellets then capture the carbon dioxide released. The CO_2 will then be sent to a salt water aquifer under the North Sea, while new forests will suck more CO_2 out of the atmosphere

① Forests cut and processed for fuel

② Power plant burns biomass; carbon-capture technology strips CO_2 from waste gases

③ Pumping station sends CO_2 down into geological storage site

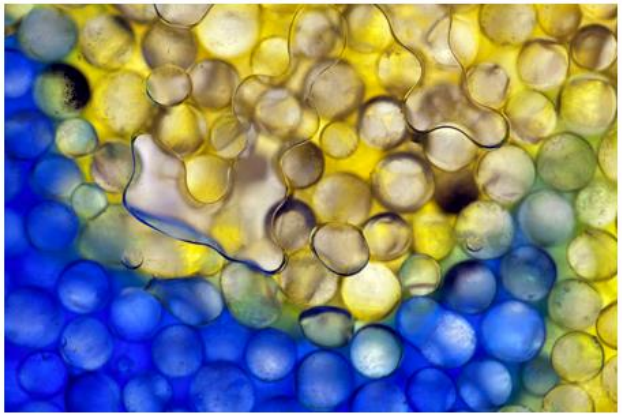
④ New trees absorb CO_2 from atmosphere

CO_2 stored in aquifer

PNAS

Lifetime of carbon capture and storage as a climate-change mitigation technology

Michael L. Szulczewski[a], Christopher W. MacMinn[b], Howard J. Herzog[c], and Ruben Juanes[a,d,1]



Capillary and solubility trapping are essential mechanisms to securing CO2 in deep saline aquifers. In this image, blobs of CO2 gas are immobilized by capillary trapping in glass beads saturated with water. Some of the CO2 dissolves in the water and is made visible by a pH indicator that changes from blue to yellow. Image / Michael Szulczewski, MIT

source: MIT On Balance, April 2012

NEGATIVE EMISSIONS TECHNOLOGIES

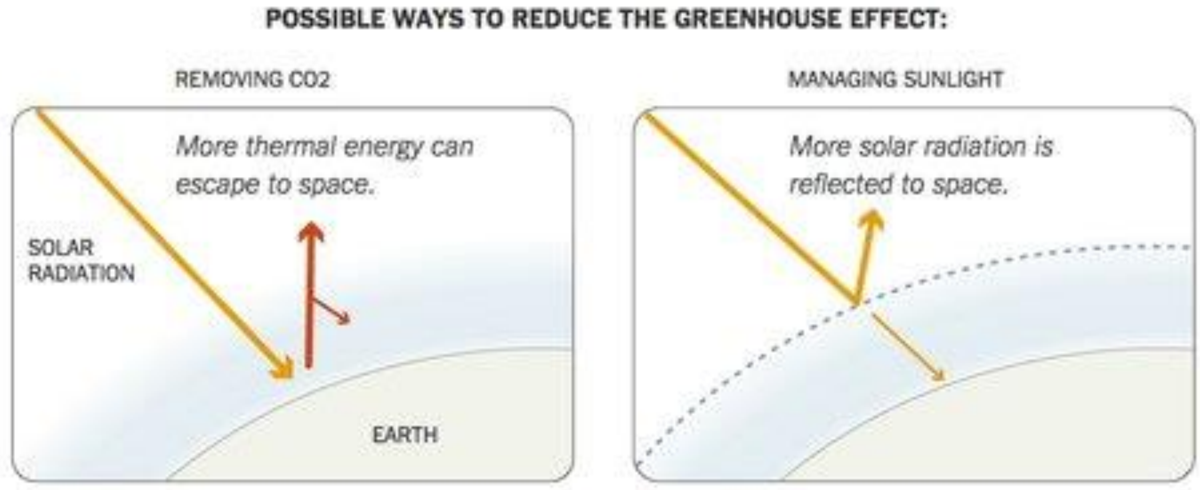
Geoengineering
(SRM vs. NET)


The New York Times

CLIMATE CHANGE

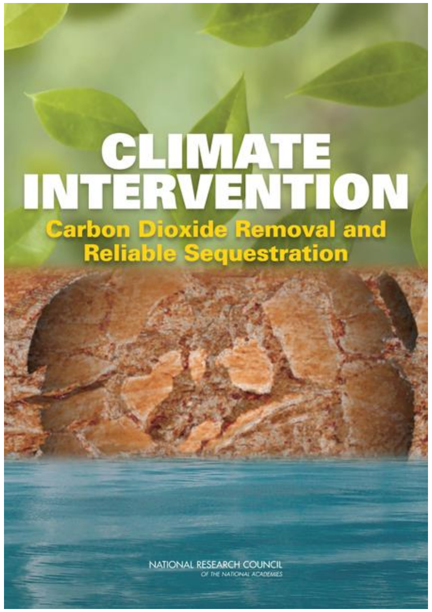
In Geoengineering Study, Science Academy Sees Merit in CO2 Removal, Risk in Reflecting Sunlight

By ANDREW C. REVKIN FEBRUARY 10, 2015 11:00 AM 196 Comments


POSSIBLE WAYS TO REDUCE THE GREENHOUSE EFFECT:

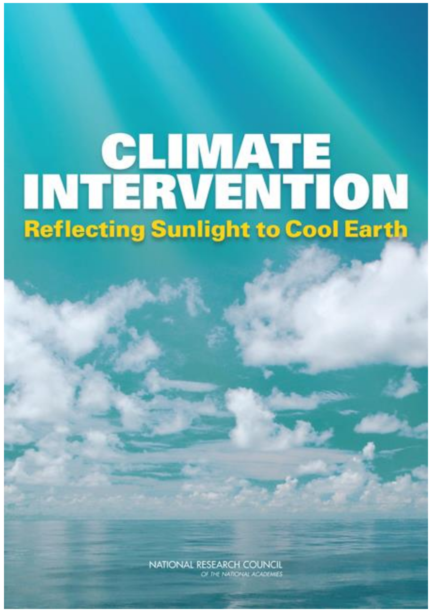
One approach is to remove some carbon dioxide from the atmosphere so it would trap less thermal energy.

Another is to make the atmosphere more reflective, by adding particles or altering clouds, so less heat is trapped.


CLIMATE INTERVENTION

Carbon Dioxide Removal and Reliable Sequestration

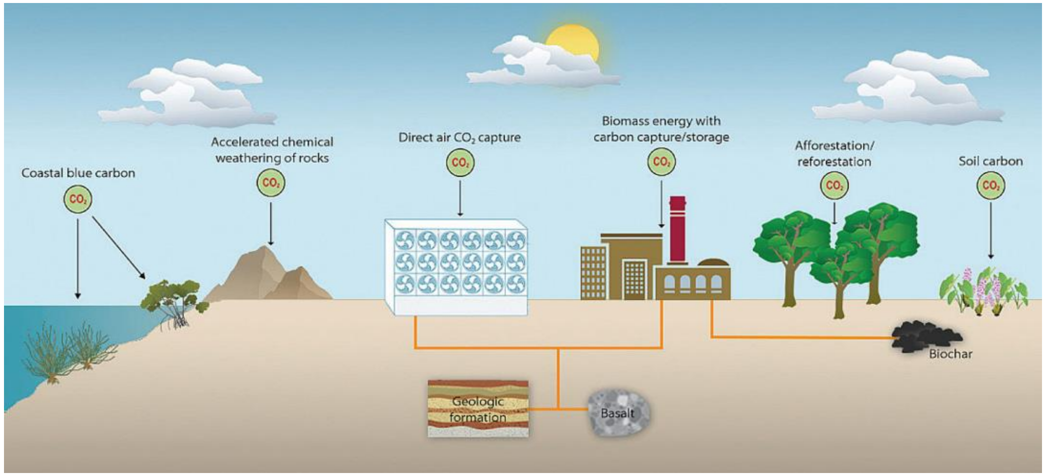
NATIONAL RESEARCH COUNCIL OF THE NATIONAL ACADEMIES


CLIMATE INTERVENTION

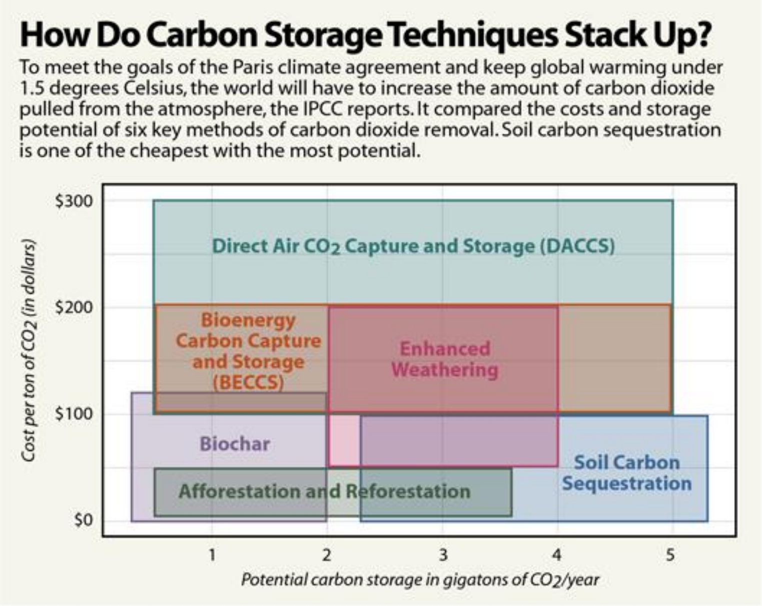
Reflecting Sunlight to Cool Earth

NATIONAL RESEARCH COUNCIL OF THE NATIONAL ACADEMIES

Technologies



source: National Academies Press, 2019

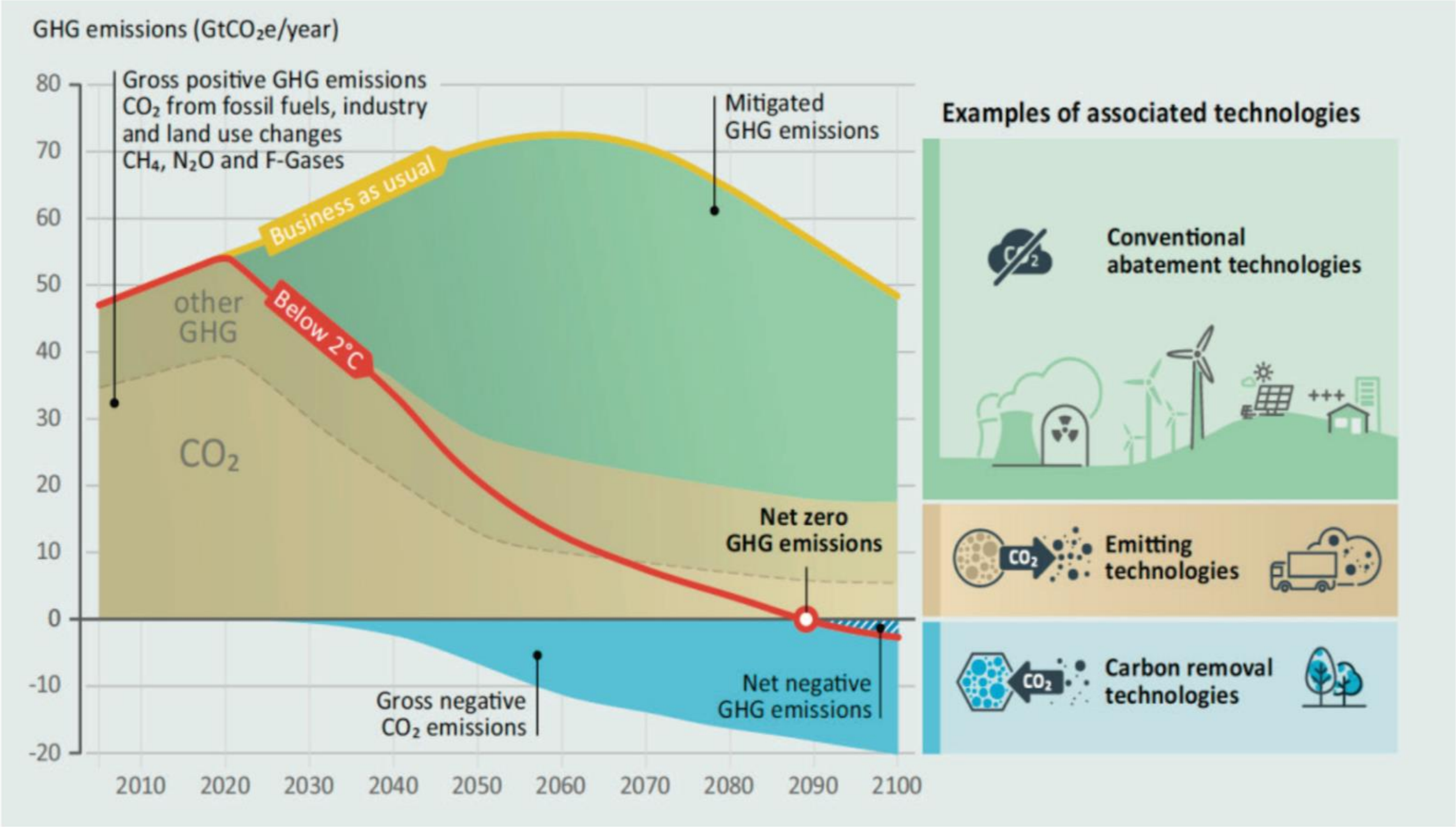


How Do Carbon Storage Techniques Stack Up?

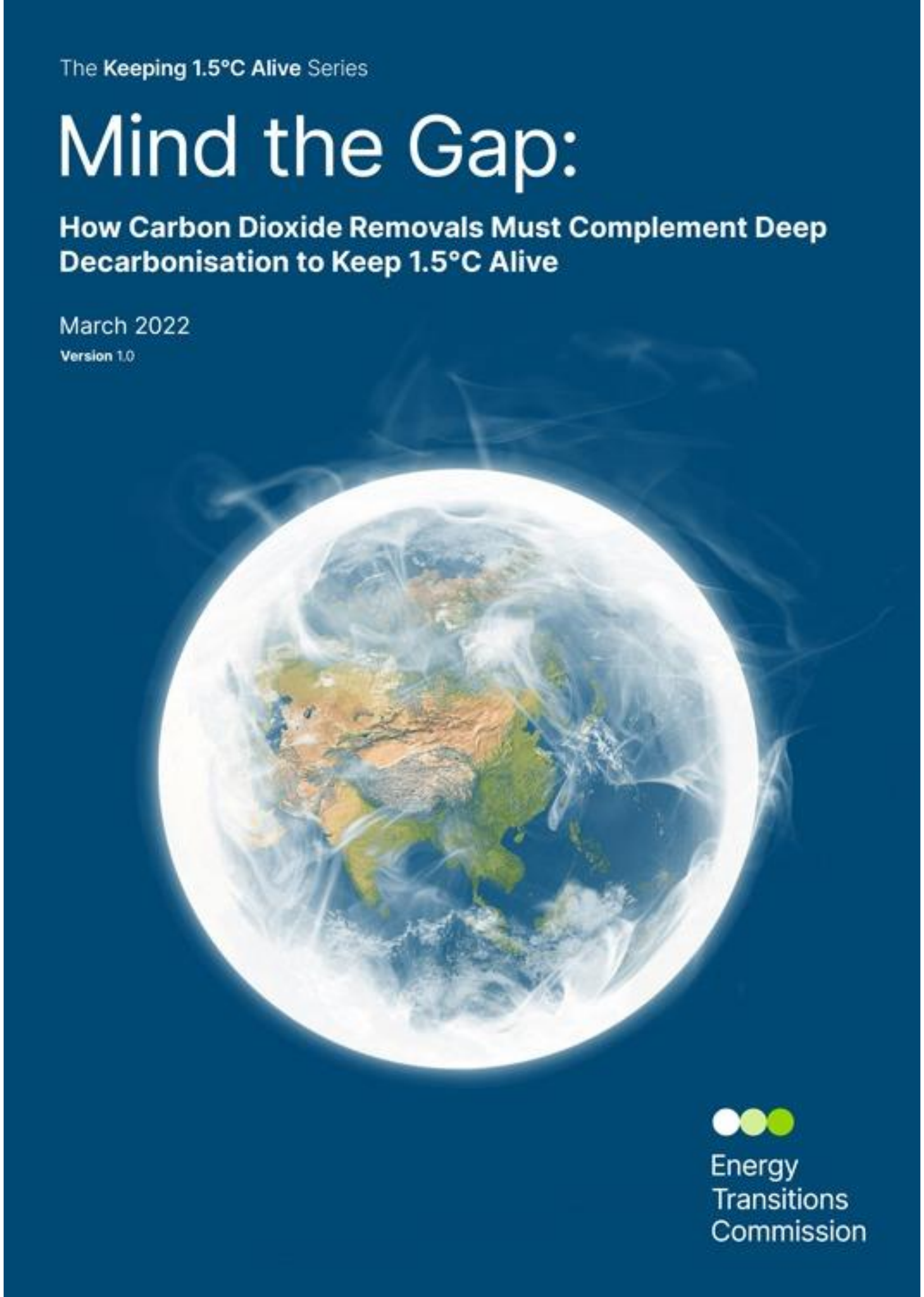
To meet the goals of the Paris climate agreement and keep global warming under 1.5 degrees Celsius, the world will have to increase the amount of carbon dioxide pulled from the atmosphere, the IPCC reports. It compared the costs and storage potential of six key methods of carbon dioxide removal. Soil carbon sequestration is one of the cheapest with the most potential.

SOURCE: IPCC

InsideClimate News



source: National Academies Press, 2019



The **Keeping 1.5°C Alive** Series

Mind the Gap:

How Carbon Dioxide Removals Must Complement Deep Decarbonisation to Keep 1.5°C Alive

March 2022
Version 1.0

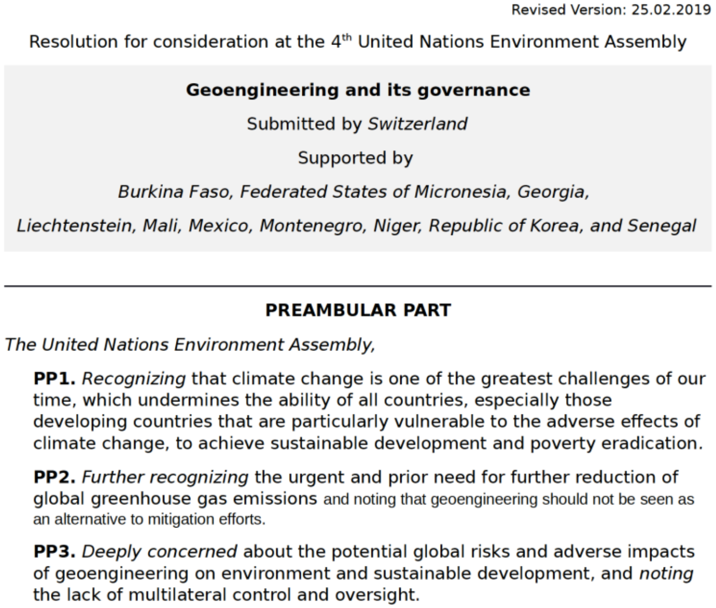
Energy
Transitions
Commission

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Negative emissions technologies

In May 2017, a number of scientists working in Switzerland addressed the public in a white paper in which they argued that an open societal conversation on the role of negative emissions technologies (NETs) and solar radiation management (SRM) in achieving internationally agreed climate targets was overdue. Their analysis is based on the science underpinning the Paris Agreement. What is Switzerland's position in response to these new policy imperatives aimed at mitigating climate change?

UNEA
United Nations Environment Assembly
of the United Nations Environment Programme



Revised Version: 25.02.2019

Resolution for consideration at the 4th United Nations Environment Assembly

Geoengineering and its governance

Submitted by *Switzerland*

Supported by

Burkina Faso, Federated States of Micronesia, Georgia,

Liechtenstein, Mali, Mexico, Montenegro, Niger, Republic of Korea, and Senegal

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PREAMBULAR PART

The United Nations Environment Assembly,

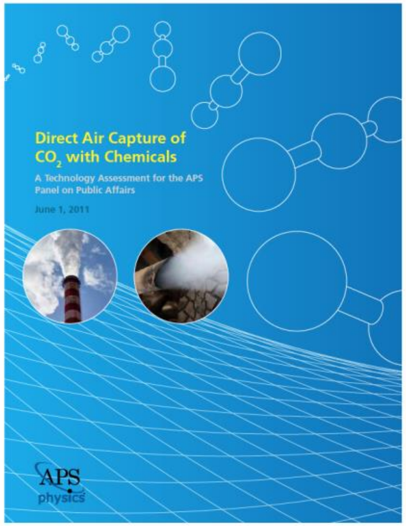
PP1. *Recognizing* that climate change is one of the greatest challenges of our time, which undermines the ability of all countries, especially those developing countries that are particularly vulnerable to the adverse effects of climate change, to achieve sustainable development and poverty eradication.

PP2. *Further recognizing* the urgent and prior need for further reduction of global greenhouse gas emissions and noting that geoengineering should not be seen as an alternative to mitigation efforts.

PP3. *Deeply concerned* about the potential global risks and adverse impacts of geoengineering on environment and sustainable development, and *noting* the lack of multilateral control and oversight.

https://www.bafu.admin.ch/bafu/en/home/topics/climate/info-specialists/climate-target2050/negative-emissionstechnologien.html
https://www.scientificamerican.com/article/u-s-blocks-u-n-resolution-on-geoengineering/

Reports/reviews on NET

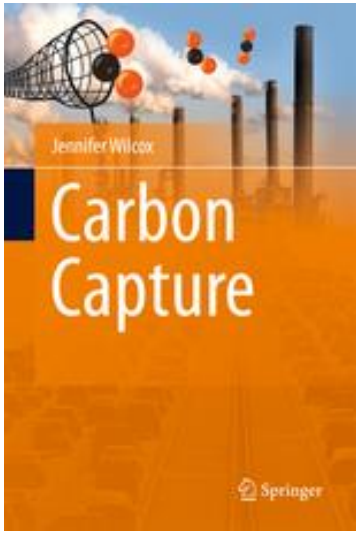


Direct Air Capture of CO_2 with Chemicals

A Technology Assessment for the APS Panel on Public Affairs

June 1, 2011

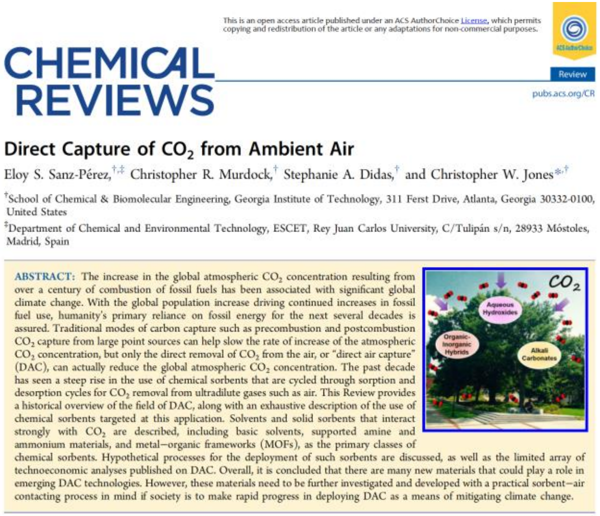
APS physics



Jennifer Wilcox

Carbon Capture

Springer



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CHEMICAL REVIEWS

Review

pubs.acs.org/CR

Direct Capture of CO_2 from Ambient Air

Eloy S. Sanz-Pérez,[†,‡] Christopher R. Murdock,[†] Stephanie A. Didas,[†] and Christopher W. Jones[*,†]

[†]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, Georgia 30332-0100, United States

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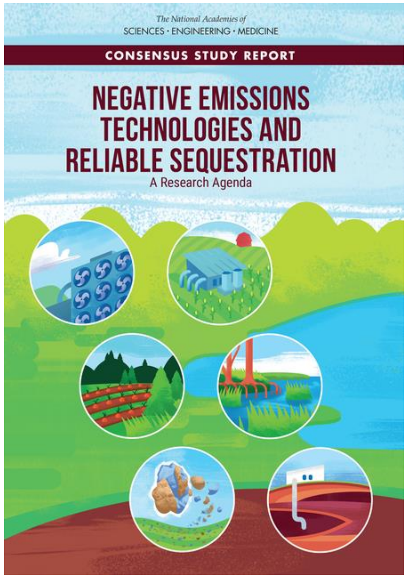
ABSTRACT: The increase in the global atmospheric CO_2 concentration resulting from over a century of combustion of fossil fuels has been associated with significant global climate change. With the global population increase driving continued increases in fossil fuel use, humanity's primary reliance on fossil energy for the next several decades is assured. Traditional modes of carbon capture such as precombustion and postcombustion CO_2 capture from large point sources can help slow the rate of increase of the atmospheric CO_2 concentration, but only the direct removal of CO_2 from the air, or "direct air capture" (DAC), can actually reduce the global atmospheric CO_2 concentration. The past decade has seen a steep rise in the use of chemical sorbents that are cycled through sorption and desorption cycles for CO_2 removal from ultradilute gases such as air. This Review provides a historical overview of the field of DAC, along with an exhaustive description of the use of chemical sorbents targeted at this application. Solvents and solid sorbents that interact strongly with CO_2 are described, including basic solvents, supported amine and ammonium materials, and metal–organic frameworks (MOFs), as the primary classes of chemical sorbents. Hypothetical processes for the deployment of such sorbents are discussed, as well as the limited array of technoeconomic analyses published on DAC. Overall, it is concluded that there are many new materials that could play a role in emerging DAC technologies. However, these materials need to be further investigated and developed with a practical sorbent–air contacting process in mind if society is to make rapid progress in deploying DAC as a means of mitigating climate change.

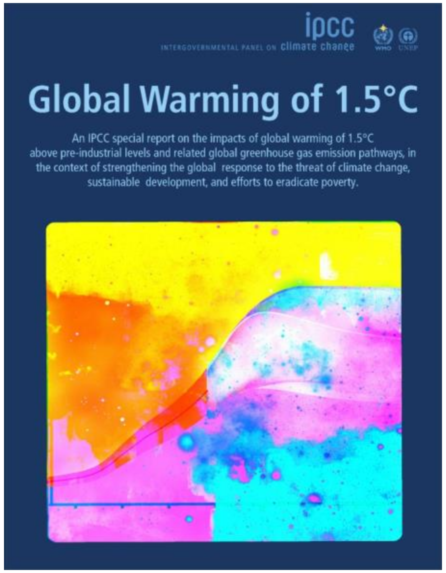


The National Academies of SCIENCES · ENGINEERING · MEDICINE

CONSENSUS STUDY REPORT

NEGATIVE EMISSIONS TECHNOLOGIES AND RELIABLE SEQUESTRATION

A Research Agenda



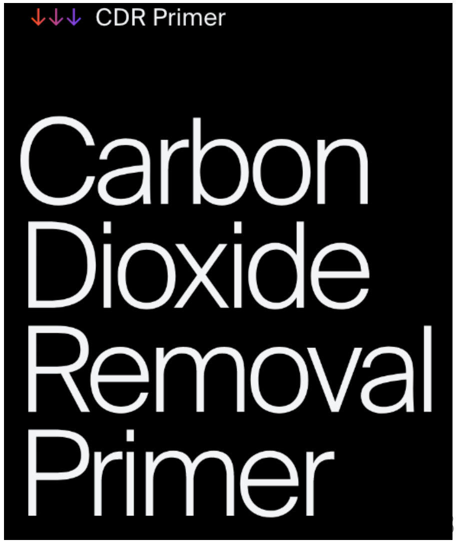
ipcc

INTERGOVERNMENTAL PANEL ON climate change

WHO UNEP

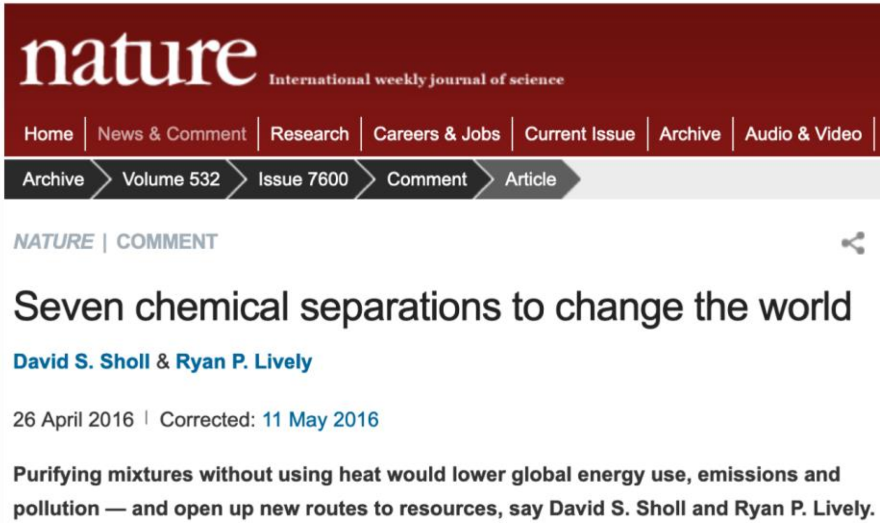
Global Warming of 1.5°C

An IPCC special report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty.



↓↓↓ CDR Primer

Carbon Dioxide Removal Primer



NATURE | COMMENT

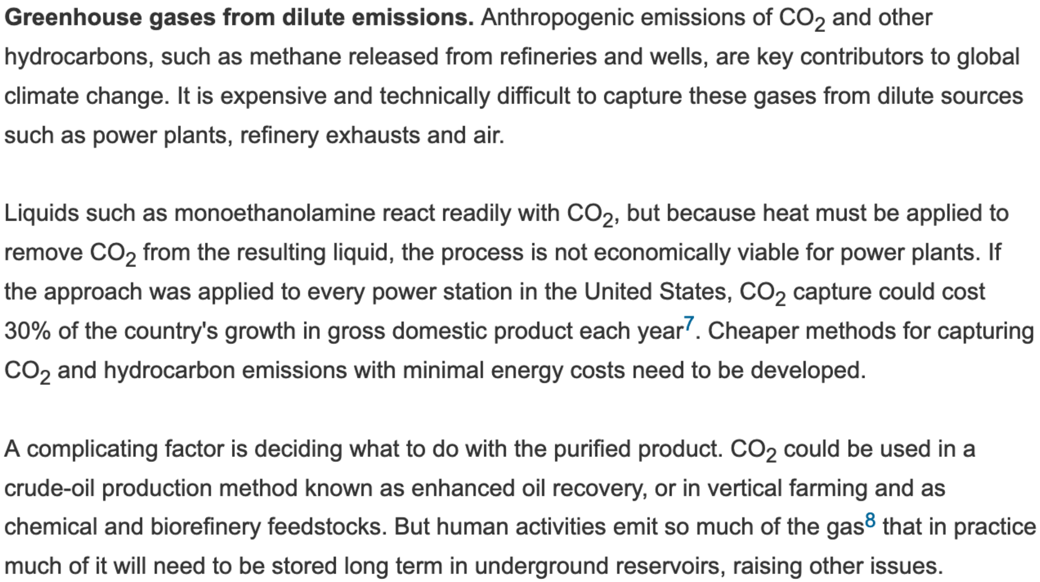
Seven chemical separations to change the world

David S. Sholl & **Ryan P. Lively**

26 April 2016 | Corrected: 11 May 2016

Purifying mixtures without using heat would lower global energy use, emissions and pollution — and open up new routes to resources, say David S. Sholl and Ryan P. Lively.

source: swissinfo.ch
(Climeworks)



Greenhouse gases from dilute emissions. Anthropogenic emissions of CO_2 and other hydrocarbons, such as methane released from refineries and wells, are key contributors to global climate change. It is expensive and technically difficult to capture these gases from dilute sources such as power plants, refinery exhausts and air.

Liquids such as monoethanolamine react readily with CO_2, but because heat must be applied to remove CO_2 from the resulting liquid, the process is not economically viable for power plants. If the approach was applied to every power station in the United States, CO_2 capture could cost 30% of the country's growth in gross domestic product each year[7]. Cheaper methods for capturing CO_2 and hydrocarbon emissions with minimal energy costs need to be developed.

A complicating factor is deciding what to do with the purified product. CO_2 could be used in a crude-oil production method known as enhanced oil recovery, or in vertical farming and as chemical and biorefinery feedstocks. But human activities emit so much of the gas[8] that in practice much of it will need to be stored long term in underground reservoirs, raising other issues.

DAC (Direct Air Capture)

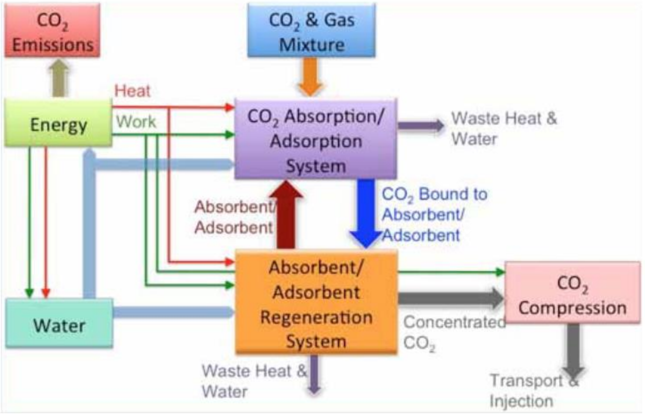


Figure 2.1 A typical system for CO_2 capture. One key component is a CO_2 absorption/adsorption system where CO_2 is chemically bound to another molecule, and removed from the gas mixture. The other key component is an adsorbent/absorbent regeneration system where CO_2 is released in a concentrated form, which is then compressed. These processes require energy (heat and work) and water. Work is in the form of electrical or mechanical power.

source: Socolow et al., 2011

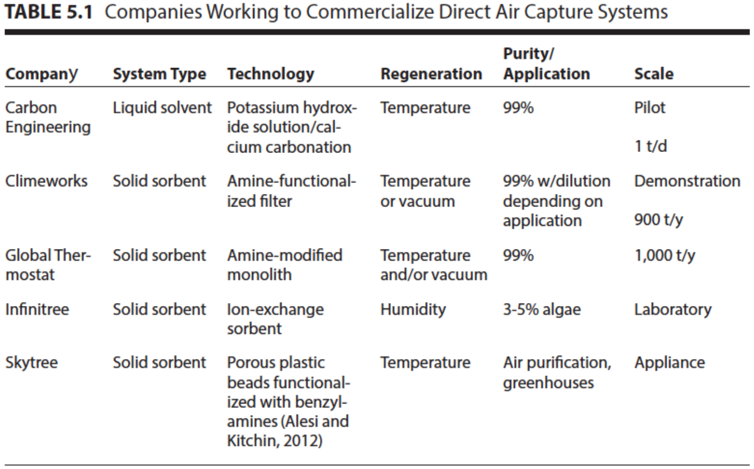


TABLE 5.1 Companies Working to Commercialize Direct Air Capture Systems

Company	System Type	Technology	Regeneration	Purity/ Application	Scale
Carbon Engineering	Liquid solvent	Potassium hydroxide solution/calcium carbonation	Temperature	99%	Pilot 1 t/d
Climeworks	Solid sorbent	Amine-functionalized filter	Temperature or vacuum	99% w/dilution depending on application	Demonstration 900 t/y
Global Thermostat	Solid sorbent	Amine-modified monolith	Temperature and/or vacuum	99%	1,000 t/y
Infinitree	Solid sorbent	Ion-exchange sorbent	Humidity	3-5% algae	Laboratory
Skytree	Solid sorbent	Porous plastic beads functionalized with benzylamines (Alesi and Kitchin, 2012)	Temperature	Air purification, greenhouses	Appliance

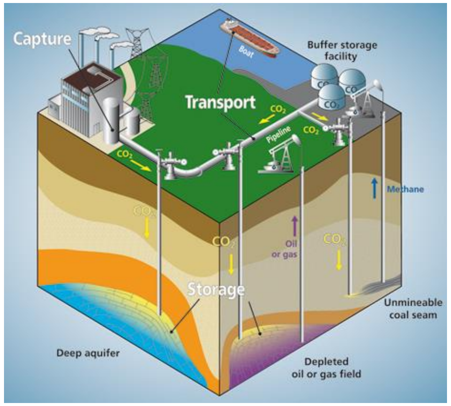
source: National Academies Press, 2019

source: Climeworks

source: Carbon Engineering

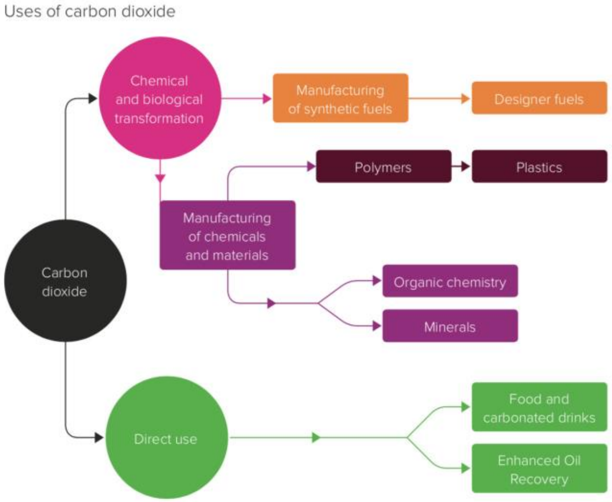
What to do with CO2

Storage



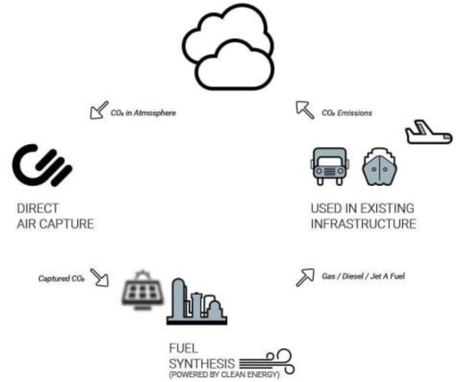
BRGM

Utilization



Royal Society

Air to fuels



Carbon Engineering

Minimum work

Ambient air

$n_1, y_1^{CO_2}, y_1^{N_2}$

Air Capture Process

$n_2, y_2^{CO_2}, y_2^{N_2}$

Processed air

$n_3, y_3^{CO_2}, y_3^{N_2}$

Product

Theoretical minimum work (reversible/isobaric/isothermal) is $W_{\text{min}} = -\Delta_{\text{mix}} G$:

$$\begin{aligned} W_{\text{min}} = -RT\,[\,& n_1 (y_1^{\text{CO}_2} \ln y_1^{\text{CO}_2} + y_1^{\text{N}_2} \ln y_1^{\text{N}_2}) \\ & - n_2 (y_2^{\text{CO}_2} \ln y_2^{\text{CO}_2} + y_2^{\text{N}_2} \ln y_2^{\text{N}_2}) \\ & - n_3 (y_3^{\text{CO}_2} \ln y_3^{\text{CO}_2} + y_3^{\text{N}_2} \ln y_3^{\text{N}_2})\,] \end{aligned}$$

Per mole of CO_2 removed:

$$w_{\text{min}} = W_{\text{min}} / (n_3 y_3^{\text{CO}_2})$$

Example:

- $y_1^{\text{CO}_2} \sim 0.04\%$ (400 ppm)
- $y_3^{\text{CO}_2} \sim 99\%$
- $w_{\text{min}} \sim 20\text{kJ/mol}_{\text{CO}_2}$

source:
Keith, *Clim. Change*, 2006
Kulkarni and Sholl, *I&EC Res.*, 2012

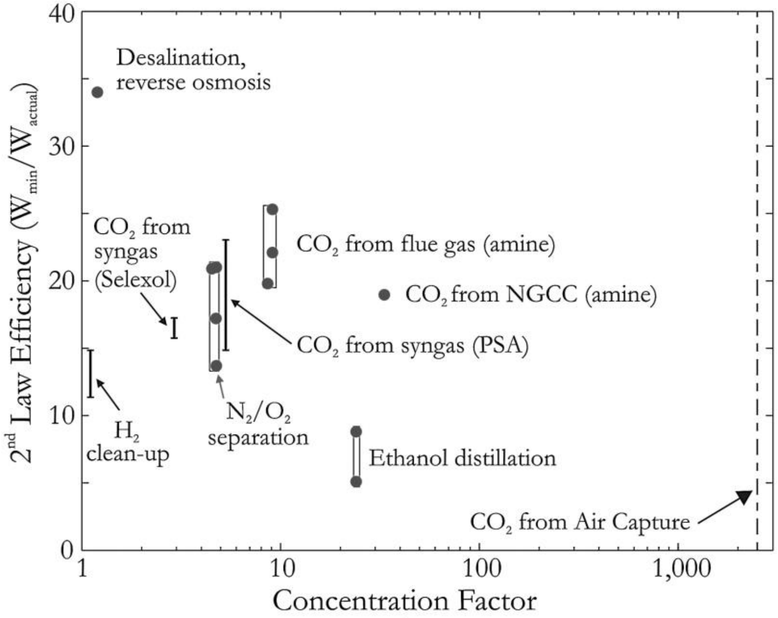
Efficiency

Real required work depends on inefficiencies in processes performing the separation.

Second-law efficiency:

$$\eta = w_{\text{min}} / w_{\text{real}}$$

House et al., *PNAS*, 2011



Empirical relationship between the concentration factor of industrial separation processes vs. the achieved second-law efficiency of those processes. Processes include separation of impurities from H_2 after steam reforming and CO_2 removal (H_2 cleanup); separation of water from brine (desalination); separation of CO2 from syngas in an Integrated Gasification Combined Cycle power plant [CO_2 from syngas (Selexol)]; separation of CO_2 from syngas after steam reforming [CO_2 from syngas (PSA)]; production of oxygen from air (N_2/O_2 separation); separation of CO_2 from coal power plant exhaust [CO_2 from flue gas (amine)]; separation of CO_2 from natural gas power plant exhaust [CO_2 from NGCC (amine)]; and separation of ethanol and water (ethanol distillation). Dots and boxes outline scatter in published reports, and lines indicate upper and lower bounds on calculations done on the basis of partial information in published reports.

Example systems

Prog. Energy **3** (2021) 032001

TOPICAL REVIEW

Progress in Energy

A review of direct air capture (DAC): scaling up commercial technologies and innovating for the future

Noah McQueen[1], Katherine Vaz Gomes[1], Colin McCormick[2], Katherine Blumanthal[3], Maxwell Pisciotta[1] and Jennifer Wilcox[1,*]

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[2] Science, Technology and International Affairs Program, Edmund A. Walsh School of Foreign Service, Georgetown University, Washington, DC, United States of America

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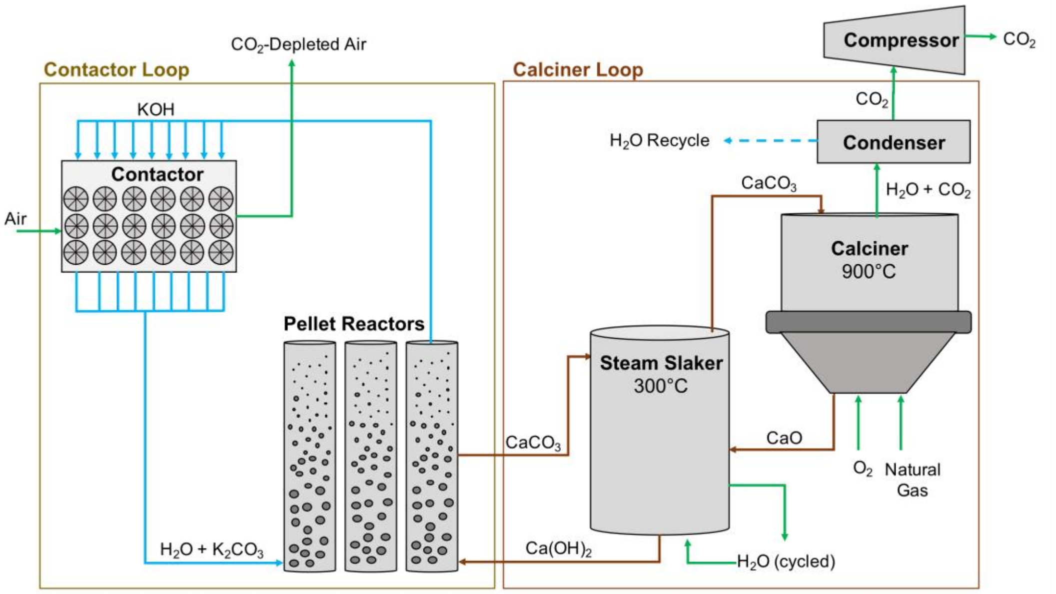


Figure 1. Representative process flow diagram for the solvent process. Here, green lines represent gaseous flows, blue lines liquid flows and brown lines solid flows. The H_2O streams undergo temperature changes throughout the process that are not represented in this simplified diagram.

solvent-based DAC

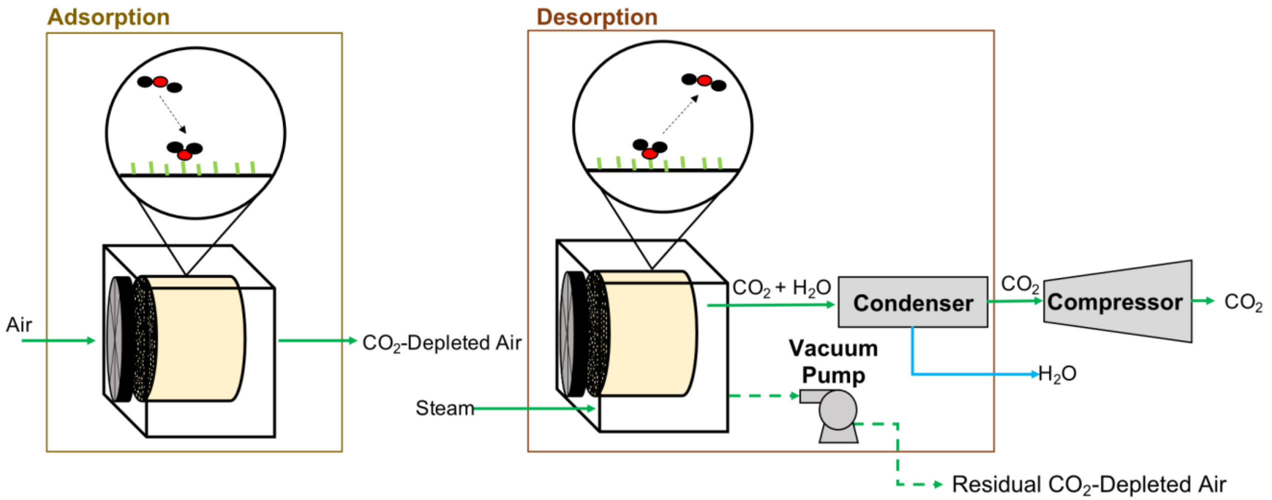
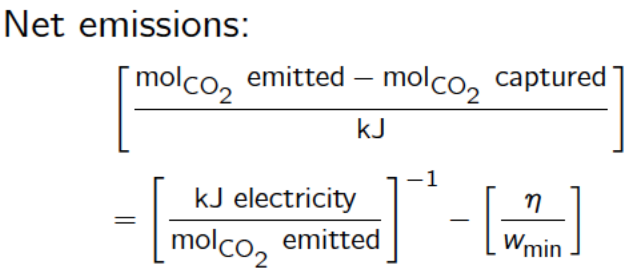


Figure 2. Representative process flow diagram for solid sorbent DAC. The adsorption and desorption processes for the solid sorbent process are performed in batch, with each composed of multiple process steps. Here, green lines represent gaseous flows and blue lines liquid flows. The dashed green line from the contactor to the vacuum pump represents the initial phase of desorption where residual air is removed from the contactor to prevent dilution of the produced CO_2 after evolution from the sorbent.

sorbent-based DAC

Net emissions



Net emissions:

$$\left[\frac{\text{mol}_{CO_2}\text{ emitted} - \text{mol}_{CO_2}\text{ captured}}{\text{kJ}}\right] = \left[\frac{\text{kJ electricity}}{\text{mol}_{CO_2}\text{ emitted}}\right]^{-1} - \left[\frac{\eta}{w_{\text{min}}}\right]$$

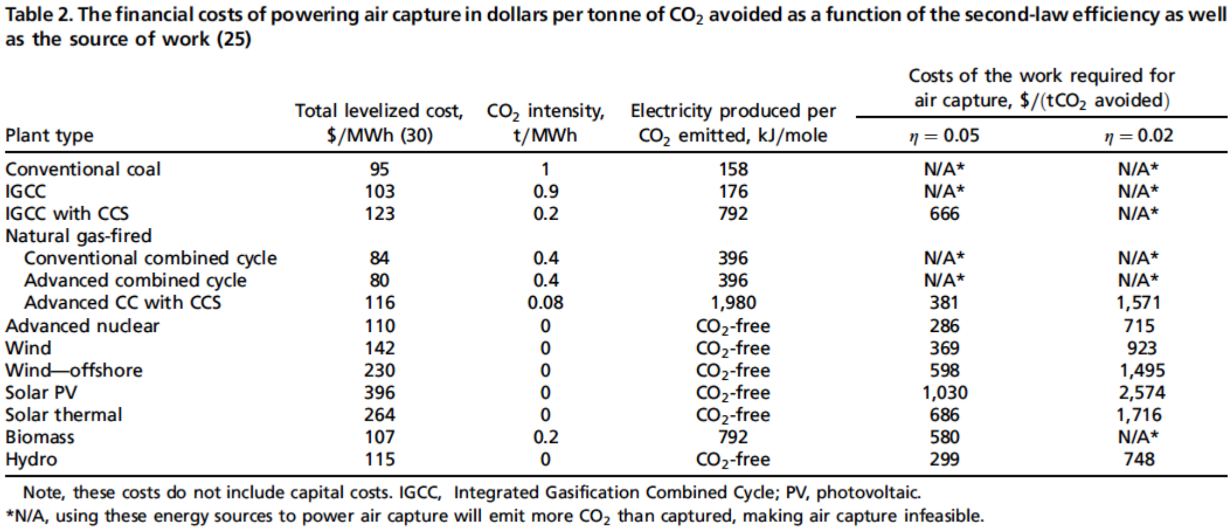


Table 2. The financial costs of powering air capture in dollars per tonne of CO_2 avoided as a function of the second-law efficiency as well as the source of work (25)

Plant type	Total levelized cost, \$/MWh (30)	CO_2 intensity, t/MWh	Electricity produced per CO_2 emitted, kJ/mole	Costs of the work required for air capture, $\$/(tCO_2$ avoided)	
				$\eta = 0.05$	$\eta = 0.02$
Conventional coal	95	1	158	N/A*	N/A*
IGCC	103	0.9	176	N/A*	N/A*
IGCC with CCS	123	0.2	792	666	N/A*
Natural gas-fired					
Conventional combined cycle	84	0.4	396	N/A*	N/A*
Advanced combined cycle	80	0.4	396	N/A*	N/A*
Advanced CC with CCS	116	0.08	1,980	381	1,571
Advanced nuclear	110	0	CO_2-free	286	715
Wind	142	0	CO_2-free	369	923
Wind—offshore	230	0	CO_2-free	598	1,495
Solar PV	396	0	CO_2-free	1,030	2,574
Solar thermal	264	0	CO_2-free	686	1,716
Biomass	107	0.2	792	580	N/A*
Hydro	115	0	CO_2-free	299	748

Note, these costs do not include capital costs. IGCC, Integrated Gasification Combined Cycle; PV, photovoltaic.

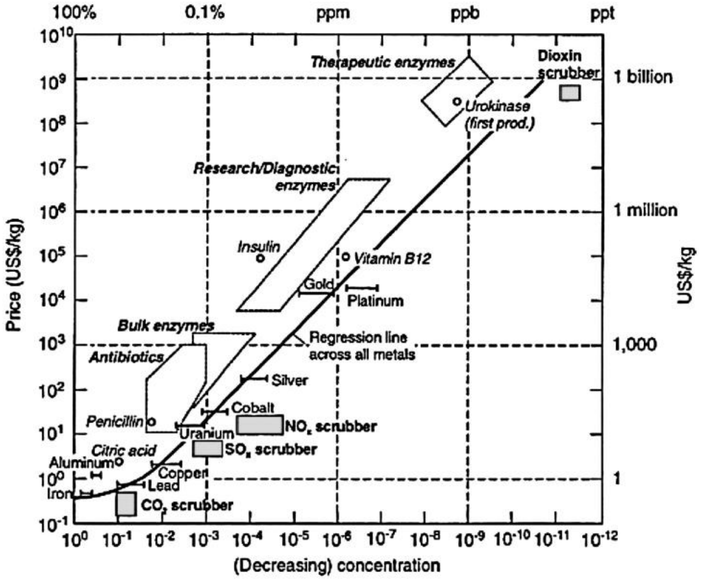
*N/A, using these energy sources to power air capture will emit more CO_2 than captured, making air capture infeasible.

House et al., *PNAS*, 2011

House et al., *PNAS*, 2011

Cost

- Sherwood plot relates the market price of a substance to its initial dilution.
- Cost of separation approx. scales inversely with initial concentration (requirements for handling greater quantities of material).
- This assumes “scaling up” of existing technologies and does not consider new technologies.



House et al., *PNAS*, 2011

Initial estimates: \$600-1000/tCO_2
Climeworks implementation: \$600/tCO_2
Carbon Eng. proposed: \$100-250/tCO_2

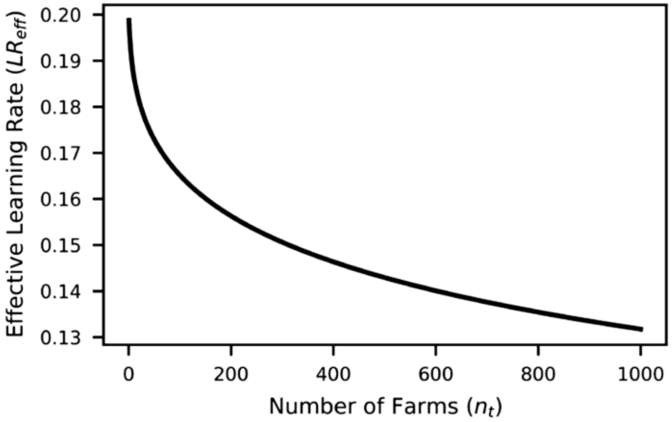
I&EC research
Industrial & Engineering Chemistry Research

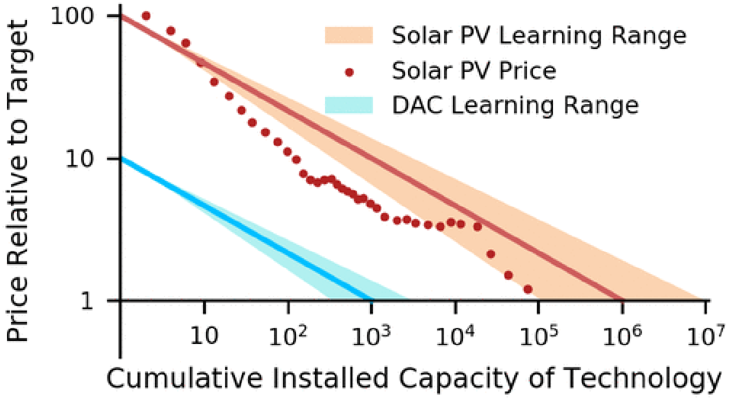
https://doi.org/10.1021/acs.iecr.0c04839
Ind. Eng. Chem. Res. 2021, 60, 8196−8208

pubs.acs.org/IECR
Article

Buying down the Cost of Direct Air Capture

Klaus S. Lackner* and Habib Azarabadi





Learning rate:

- (empirical) percentage reduction in cost of manufacturing for every doubling of cumulative output

Improvements in:

- production process
- technological breakthroughs
- supply chain

Target: \$100/ton is target (Price of CO_2 used for commercial purposes: \$65 to \$110/ton)

Further reading

- Cooper, C. David, and F. C. Alley. *Air Pollution Control: A Design Approach*. Waveland Press Inc, 2011.
- Flagan, R. C and Seinfeld, J. H. Fundamentals of Air Pollution Engineering, Prentice Hall, Inc., New Jersey, 1988. Available online: http://authors.library.caltech.edu/25069/
- Wark, Kenneth, Cecil Francis Warner, and Wayne T. Davis. *Air Pollution: Its Origin and Control*. Addison-Wesley, 3rd ed., 1998.