A Fair Share: Doing the Math on Individual Consumption and Global Warming

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Contents

Chapter 3

Essential background

In this chapter, I delve more deeply into several topics of major importance to the rest of the book, beginning with a brief primer on mathematical units and the differences between energy and various emissions metrics, with an especial focus on the global warming potential (GWP) metric and its mathematical description for various GHGs, a review of the properties and emissions sources of most major anthropogenic radiative forcers (i.e. substances released into the atmosphere that have a global warming *or* cooling effect, and include all GHGs), and major carbon stocks and sinks.

Of particular importance in the earlier part of this chapter is a discussion of the 1987 Montreal Protocol and the ozone-depleting halocarbons (e.g. CFCs and HCFCs) widely used as refrigerants, propellants, and for other industrial uses. The Montreal Protocol, by far the most successful international environmental treaty, has not only averted a crisis in the ozone layer by directing the ongoing phase-out of these substances (especially CFCs), but has also (incidentally) avoided much radiative forcing (i.e. global warming) that would otherwise have occurred, for the Montreal gases are also extremely potent greenhouse gases.

A key historical lesson also comes from the recognition that early consumer behavior was important to the CFC phase-out: the possible harms of CFCs were first described in 1974, and this "1974 warning" resulted in widespread voluntary consumer changes and some national-level restrictions (but no international action) that likely avoided around 50% of the CFC emissions that would have otherwise occurred until definitive international action occurred with Montreal in 1987. Thus, consumer changes markedly lowered the overall CFC burden on the atmosphere, and awareness and willingness to change among the consumer class was likely essential to Montreal being politically feasible. There is a clear parallel to climate change: while high-level international action and broad technological changes were necessary to ultimately phase-out CFCs, and the same is likely true for GHGs, the task was greatly abetted by early consumer action, which is almost certain to be true for climate change as well.

The latter part of this chapter focuses more on fuels, especially fossil fuels, beginning with an introduction to the process of combustion, by which various hydrocarbons are converted to heat, water, and CO_2, along with other byproducts. The intrinsic chemical makeup of different fossil fuels governs their energy (heat) content, as well as the amount of CO_2 generated per kWh in a predictable manner, with a higher hydrogen:carbon ratio giving more energy and lower CO_2/kWh. I then discuss the geologic processes by which fossil fuels come into being, focusing especially upon unconventional natural gas and oil that is increasingly extracted via hydrofracking, and conclude with an overview of M. King Hubbert's famous, and still highly relevant, "Peak Oil" theory. Next, various biofuels (corn ethanol, soy biodiesel, and wood) and their scalability as replacements for major fossil fuels is addressed, and we see that none are viable replacements at anything approaching current US energy use, although wind and solar

clearly are. The chapter closes with an overview of historical primary energy consumption in the US, demonstrating the remarkable transition from a wood-fired world to one powered almost entirely by fossil fuels in just the last century and a half.

3.1   Some notes on units

There are two major systems of measurement, the metric system, known in its modern incarnation as the International System of Units, or SI, from the French Système International d'Unités, and the British (or "Imperial") system, familiar principally to Americans and member states of the Commonwealth. Essentially all base calculations in this book are performed using metric units, but because some British units are so prevalent, I sometimes present results converted to British units. Most prominently, I have chosen to use miles for distance and degrees Fahrenheit for temperature, as well as gallons as the base unit for fuel volumes. I occasionally use acres for land area as well, and horsepower for power. Most other units are given in metric; of special note, emissions factors are always given in metric terms. British (or "short") tons are never used, and the term "tonne" is synonymous with metric ton (1,000 kg).

Throughout this book, comfort with the metric system of units, scientific notation, and converting between different orders of magnitude is a necessity for the fullest comprehension. The most natural unit for household CO_2-equivalent emissions is the metric ton, or "tonne," equivalent to 1,000 kg or 10^6 grams, and thus can also be referred to as a *megagram* (Mg); this is precisely what I do. A Mg consists of 1,000 kilograms (kg), and a kg in turn is equal to 1,000 grams (g). Depending upon the context, any of these units may be most natural. For example, burning a gallon of gasoline generates about 11 $kgCO_2e$, while burning 500 gallons generates around 5,500 $kgCO_2e$, more concisely given as 5.5 $MgCO_2e$. With this, we dip but a toe in the sea of dimensional analysis, and far more treacherous mathematical waters lie ahead: reader, consider thyself warned.

3.2   Emissions, energy, and primary energy

I take this opportunity to emphasize the differences between several terms that appear throughout this book, both to improve understanding, and to avoid some common pitfalls in thinking. My primary focus in the book is CO_2-equivalent emissions (CO_2e), generally measured via the global warming potential (GWP) metric, which, as described below, measures the warming effect of a substance (or behavior) over 100 years and rescales this in terms of the warming effect of a pulse emission of CO_2 over 100 years. The 100-year horizon is ultimately arbitrary, and 20-year, 50-year, etc. GWPs may also be described, and when applicable I label such values GWP_x, where x is the time-horizon.

Sometimes carbon (C), *per se*, and carbon dioxide (CO_2) are confused. Carbon has a molecular weight of about 12, while CO_2 has a molecular weight of 44, and thus when emissions are given in units of C, they must be converted to CO_2 by a scaling factor of 44/12, e.g. 1 MgC = 44/12 $MgCO_2$. Adding to potential confusion, "carbon emissions" and related terminology are frequently used in a generic sense, referring to greenhouse gases in general. While in prose I sometimes use generic terminology, all numbers are accompanied by precise units, so, for example, 1 MgC, 1 $MgCO_2$, and 1 $MgCO_2e$ mean precisely 1 tonne of carbon (C), 1 tonne CO_2, and 1 tonne CO_2-equivalent (and in this last case the physical component gases may be anything, and further, unless otherwise stated this means CO_2-equivalents over a 100-year timeframe), respectively.

Carbon emissions are strongly linked to fossil energy use, and it is a common error in the popular literature to confuse emissions with energy. Energy is typically measured in either joules

(J), or, more commonly, watt-hours (Wh) or kilowatt-hours (kWh). Energy is the integral (or summation) of power, and so 1 kWh is the energy used when drawing 1 kW of power over 1 hour. Now in general, any use of energy has some associated carbon intensity, which we may quantify in $kgCO_2e/kWh$, and this quantity may vary over orders of magnitude, being, for example, about 0.01 $kgCO_2e/kWh$ for wind-derived electricity and 1 $kgCO_2e/kWh$ for coal-fired electricity, respectively. Further, emissions intensities tend to be lower for direct fuel use, around 0.2–0.3 $kgCO_2e/kWh$ for typical fossil fuels, but in the 0.6–1.1 $kgCO_2e/kWh$ range for fossil-derived electricity (including all lifecycle emissions). But note that we are here comparing two different forms of energy, thermal (heat) in the former case, and electrical in the latter; sometimes the notation kWh(t) and kWh(e) is used to distinguish between the two. Electrical energy is "higher quality," and this leads us to the concept of *primary energy*, which is the energy contained in raw fuel before any downstream transformation.

In typical fossil fuel generating plants, only 30–45% of the thermal energy contained in fuel is converted to electrical energy (the "thermal efficiency"). This electrical energy is then distributed at a loss and devoted towards various end uses, at varying efficiencies. For example, suppose we used a motor to convert electricity to motion with 85% efficiency, but if the electricity was derived from a gas generator at 40% thermal efficiency and 6.5% was lost in the distribution system, then our primary energy efficiency would be just $85\% \times 40\% \times 6.5\% = 31.8\%$. Several renewable energy sources yield electricity at the primary level, e.g. hydropower, solar, and wind. Therefore, when we do calculations, as in Section 4.14, on the renewable energy resources needed to replace all global primary energy, renewables suffer a penalty in a straight one-to-one comparison, as much fossil primary energy is lost in transformation to electricity or other ends. The idea of primary energy is also important when comparing the efficiency of, e.g., electric and gasoline-based vehicles, or gas and electric heaters.

3.3 The GWP metric and mathematics, oh my

As already discussed, in order to assess and compare the impact of various activities, from the individual to global scale, we must use some common unit of measurement, or metric. The fundamental metric that I will use throughout this book, in line with the IPCC, is *metric tons of carbon dioxide equivalents* ($MgCO_2e$), defined on the basis of global warming potential (GWP). Note that we use CO_2 *equivalents*. That is, there are multiple greenhouse gases, each with unique properties, but we express the effect of each on the climate in terms of an equivalent amount of CO_2. But how to do this, you may ask, and while there are several commonly used methods, no one is necessarily more "correct" than another. To further complicate matters, because different gases act over different timescales, depending on how far into the future we look, a given gas will be "equivalent" to different amounts of CO_2 at different points in time.

The standard IPCC method is to compare gases in terms of GWP, with the GWP of gas x defined as, and bear with me dear reader, the integrated *radiative forcing* (RF) due to a pulse emission of one kg divided by the integrated radiative forcing of a single kg of CO_2. To understand this sentence first requires understanding radiative forcing. Consider a kg of gaseous CO_2 spread uniformly throughout the atmosphere. This CO_2 will continuously trap some heat and we quantify the amount of heat trapped per unit time in units W m^{-2}: this quantity is the *instantaneous* radiative forcing. Note that the term radiative forcing stems from the notion that greenhouse gases trap long-wave infrared *radiation* and thereby *forces* heating of the earth. The *radiative efficiency* (RE) of a gas is the per-kg radiative forcing (W m^{-2} kg^{-1}).

Now, when a pulse of CO_2, or any other gas, is emitted, not all of it stays in the atmosphere. For many gases, the pulse decays away according to a simple exponential equation, and the rate of decay is quantified by a single parameter, the "perturbation lifetime." Formally, for some

gas x we have the fraction remaining in the atmosphere at time t, $R_x(t)$, as

$$R_x(t) = e^{-\frac{t}{\tau_x}}, \tag{3.1}$$

where τ_x is the perturbation lifetime, and the instantaneous radiative forcing at any time is

$$RF_x(t) = A_x R_x(t), \tag{3.2}$$

where A_x is the radiative efficiency. Finally, integrating RF out to some time horizon H gives us the absolute GWP (AGWP) for gas x,

$$\text{AGWP}_x(H) = \int_0^H RF_x(t)dt \tag{3.3}$$

and we then have the mathematical expression for GWP_x as the $\text{AGWP}_x/\text{AGWP}_{CO2}$ ratio,

$$\text{GWP}_x(H) = \frac{\text{AGWP}_x(H)}{\text{AGWP}_{CO2}(H)}. \tag{3.4}$$

Figure 3.1 shows the time-course of the remaining mass and integrated RF, i.e. AGWP, of a CO_2 bolus over 100 years, and further compares these time-courses to those of a methane (CH_4) bolus. Dividing the respective AGWPs at each time-point gives the CH_4 GWP at any given time horizon, also shown in Figure 3.1. We may also modify GWP values via consideration of climate-carbon feedbacks, as done in the most recent IPCC assessment [7], and while there is uncertainty, the GWP metrics including climate-carbon feedback are likely better estimates. For example, 100-year GWPs for methane are given as 28 and 30 for biogenic and fossil methane, respectively, without climate-carbon feedback, but 34 and 36 with such feedback. The GWP values for biogenic and fossil methane vary slightly because, as reviewed in Section 3.4.2, CH_4 is oxidized to CO_2 in the atmosphere. For biogenic CO_2, this is not *new* to the short-term carbon cycle, while for fossil methane this represents an additional anthropogenic warming source. I now take a moment to review the slightly more complex CO_2 pulse dynamics.

3.3.1 CO_2 pulse dynamics

In the case of a CO_2 pulse emission, over time some is absorbed into the ocean, and some is incorporated into various carbon pools such as forests, other biomass, soil organic carbon, etc., while a substantial portion will persist in the atmosphere for millennia. The method for deriving a relatively simple mathematical description of this process has been to run large-scale biophysical simulations that track the fraction of a large pulse (100 Gt) of CO_2 emitted into the atmosphere that remains over the course of a millennium. Then, a simple mathematical equation is fit to the result; the form of this equation is a sum of exponentials, each with a unique time constant. Roughly speaking, each exponential describes the incorporation into a different pool[1]. From Joos et al. [20], we have that the fraction of a CO_2 pulse remaining in the atmosphere, $R_{CO_2}(t)$, at time t (in years) is

$$R_{CO_2}(t) = a_0 + \sum_{i=1}^{3} a_i \exp\left(\frac{-t}{\tau_i}\right) \tag{3.5}$$

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[1]This mathematical form is equivalent to a "multi-compartment" pharmacokinetic model describing how the plasma concentration of a drug changes over time following injection into a human (or some unfortunate animal). The compartments are thought to represent various tissues, and the drug moves into different peripheral compartments from the plasma at different rates, analogous to the atmospheric carbon dioxide being incorporated into various terrestrial or marine carbon pools at different rates.
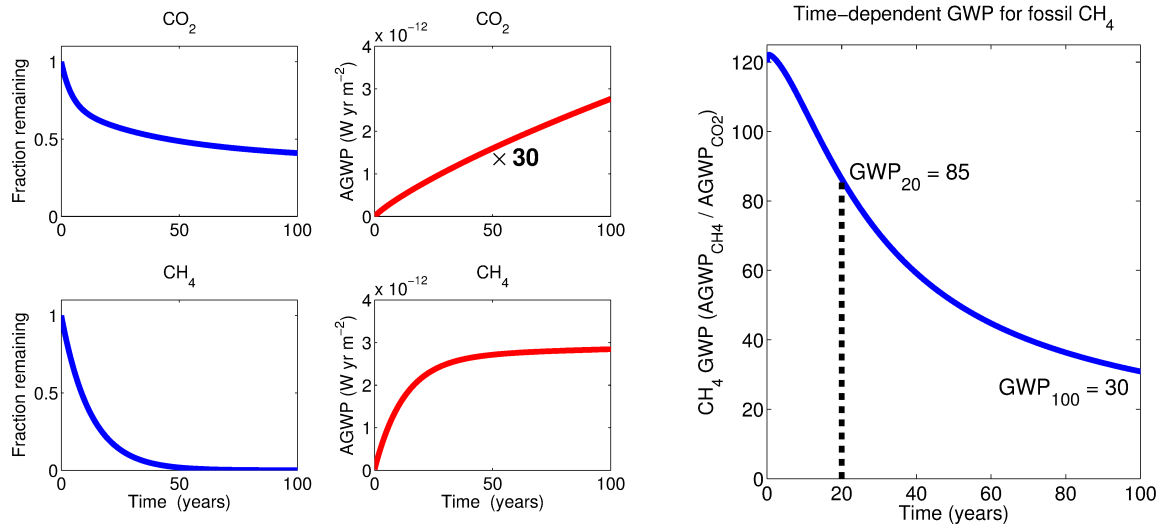
Figure 3.1: The leftmost panels show the time-courses of CO_2 (top) and fossil CH_4 (bottom) removal from the atmosphere, following a 1 kg pulse emission. We see that CO_2 is quite long-lived, while methane is cleared within a few decades. Moving to the right, we have the *integrated* RFs (AGWP) from these gases at each year, with the CO_2 AGWP inflated 30-fold to make it visually comparable to that of CH_4. Now, the AGWP for methane becomes very large initially, but, because the gas clears by the fifth decade, it then plateaus (i.e. no further warming effect), while the CO_2 AGWP steadily rises, reflecting the persistent warming effect. Dividing these two quantities shows that the relative warming effect of a CH_4 bolus, relative to CO_2, is very large in the first years and steadily declines, but is still 30 at the 100-year horizon. These calculations include the slight effect of methane oxidizing to CO_2, but omit climate-carbon feedbacks for CH_4.

The a_i parameters are given as 0.2173, 0.2240, 0.2824, and 0.2763 in ascending order, and time-constants, τ_i, are 394.4, 36.54, and 4.304 years, also in ascending order. The radiative efficiency of CO_2, A_{CO2}, is 1.37×10^{-5} W m^{-2} ppb^{-1}, or 1.7561×10^{-15} W m^{-2} kg^{-1}. This equation and RE value is used to inform Figure 3.1.

3.4   Major radiative forcers

Here I discuss major radiative forcers, i.e. those substances that exert either an atmospheric warming or cooling effect, and almost all anthropogenic alteration of the climate is thus manifested through such agents. The radiative forcing concept underlies the GWP metric, and there are several ways to define it. As above, we can consider the instantaneous radiative forcing of some species, in W m^{-2} kg^{-1}, but, in climate assessments, the more typical method is to compare the total radiative forcing attributable to a substance *relative* to a pre-industrial baseline, taken as the 1750th year of the Common Era by the IPCC. Since 1750, total anthropogenic forcing reached 2.3 W m^{-2}, on balance, in 2011 by the IPCC's estimate, driven principally by CO_2, CH_4, and several other lesser gases, and partially counteracted by cooling aerosols (mainly nitrate and sulfate) also released by the activities of industrial civilization.

Different future emissions scenarios have been defined by the IPCC on the basis of projected radiative forcing in 2100, referred to as representative concentration pathways (RCPs). A low-emissions scenario where emissions rapidly decrease after 2020 and global warming stabilizes at around a 1.5 °C increase in global mean air temperature is the RCP2.6 pathway (i.e. RF of 2.6 W m^{-2} in 2100), while a high-emissions scenario, the RCP8.5, corresponds to continuing emissions over the twenty-first century and dramatic warming; depressingly, humanity seems much more on track for the latter than the former.

Broadly speaking, radiative forcers are divided into the overlapping categories of well-mixed greenhouse gases (WMGHG) and near-term climate forcers (NTCF) [7]. The WMGHGs include CO_2, CH_4, nitrous oxide (N_2O), and some halocarbons, with the first three forming a canonical group most often considered in lifecycle assessments, while major NTCFs include methane (the only major overlapping species), ozone (O_3), aerosols (mainly sulfate (SO_4), nitrogen oxides (NO_x), and black and organic carbon), and other halocarbons. Stratospheric ozone is essential for blocking UV light, as discussed in Section 3.4.4, but O_3 is also a powerful greenhouse gas with a complex atmospheric chemistry coupled to many other radiatively active molecules, and many emissions, e.g. methane, can increase O_3 for a downstream warming effect. Note that water vapor (H_2O) is actually the largest contributor to the atmospheric greenhouse effect overall, but, in the lower atmosphere water concentration is essentially a feedback response to other greenhouse gases, and anthropogenic water emissions are trivial in magnitude compared to the background hydrologic cycle, and so it is *not* considered an anthropogenic GHG. However, statospheric H_2O emissions, e.g. from high-flying aircraft or methane oxidation, do remain in the stratosphere and exert a warming effect. Natural variation in solar irradiance (very minor), land use changes that alter surface albedo (i.e. reflectivity), and aircraft contrails and induced cloudiness also affect radiative forcing.

All the WMGHG and most of the NTCF have a net warming effect, with the major exception of several anthropogenic aerosols, which exert a powerful (if short-lived) cooling effect, partially counteracting the warming gases. It is also apropos to introduce the idea of *abundance*- and *emissions*-based radiative forcing. The former is a measure of warming strictly due to the concentration of any given substance in the atmosphere (relative to pre-industrial times), while the latter includes the downstream effects of a past emission stream. For example, methane emissions increase ozone, CO_2, and stratospheric water concentration, and so the warming attributable to methane *emissions* is greater than that due to its atmospheric abundance alone.
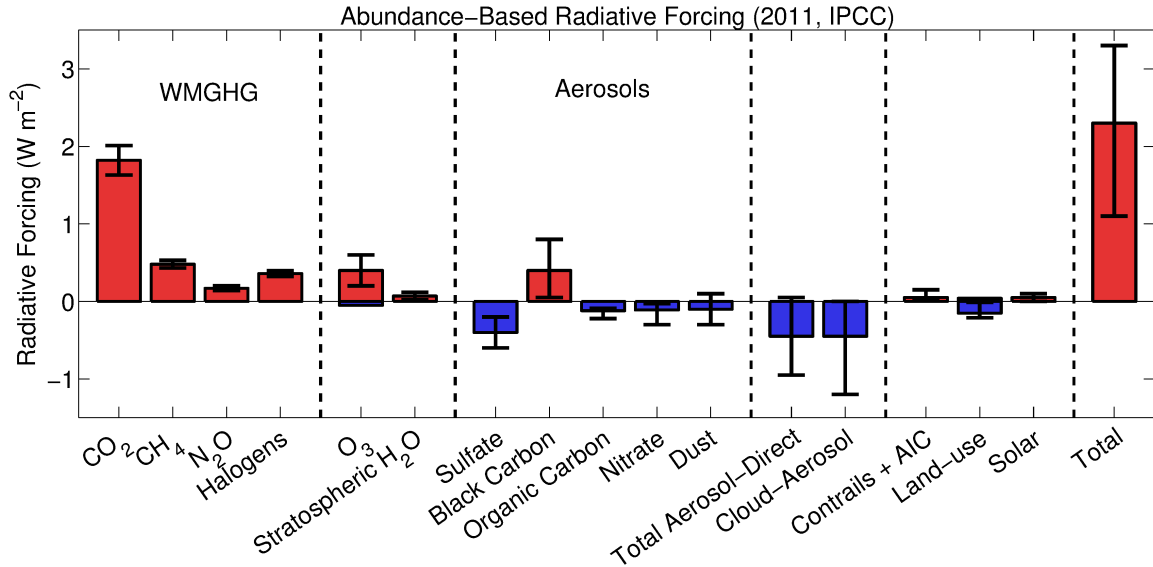
Figure 3.2: Abundance-based radiative forcing since 1750 attributable to major species, in 2011, per the fifth IPCC assessment [7].

Figures 3.2 and 3.3 summarize the IPCC's most recent estimates for abundance- and emissions-based radiative forcing. In either case, CO_2 is dominant with CH_4 second, but relative impact of CH_4 approaches 60% of CO_2's on an emissions-basis.

3.4.1 Carbon dioxide (CO_2)

Carbon dioxide is the canonical greenhouse gas, and is the dominant contributor to anthropogenic radiative forcing, on both an abundance and emissions basis. Globally, and in the US, most CO_2 emissions are attributable to fossil fuel combustion, either for energy, transportation, residential heat, or industrial activity, with CO_2 from deforestation and other land use changes contributing about 15% of CO_2 emissions in recent years [7] (but a much greater proportion during the early industrial era); cement production also directly yields 5–7% of global CO_2 [21]. There is little disagreement as to the sources and magnitude of CO_2 emissions [22], and the fundamental role of this gas in anthropogenic global warming is incontrovertible [7].

3.4.2 Methane (CH_4)

After CO_2, methane is the second most important GHG, and atmospheric concentrations have increased dramatically since preindustrial times, nearly tripling from 722 ± 25 ppb to just over 1803 ± 2 ppb in 2011 [7]. On a concentration basis, the IPCC estimated radiative forcing attributable to CH_4 at $0.48\pm.05$ W m^{-2} in 2011, about a quarter of the 1.82 ± 0.19 W m^{-2} from CO_2. However, atmospheric methane chemistry is complex, and CH_4, NO_x aerosol, hydroxyl radical (HO), and ozone chemistry are all coupled. Methane is a major ozone precursor (tropospheric ozone is a powerful greenhouse gas), oxidation by HO leads to stratospheric water and CO_2, and CH_4 enhances its own lifetime through a feedback effect upon the hydroxyl radical. After accounting for these indirect effects, on an *emissions* basis, CH_4 forcing is doubled relative to its abundance forcing, to 0.97 W m^{-2}, compared to 1.7 W m^{-2} for CO_2 (in 2011) [7, 23]. Most of this increase is attributable to ozone produced downstream of methane, and the IPCC quantifies CH_4 AGWP at year H as
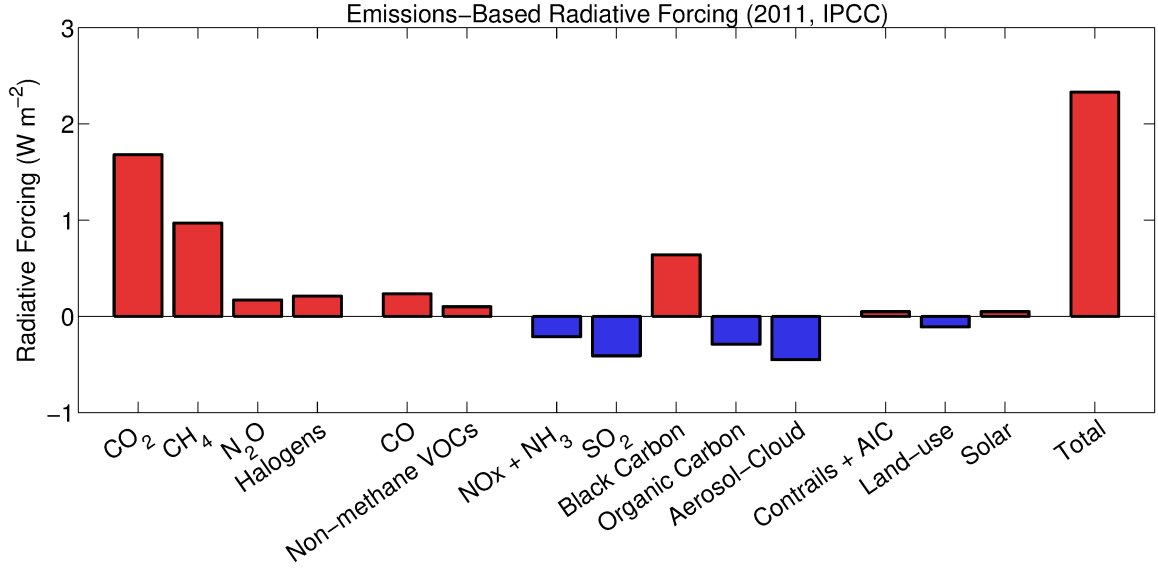
Figure 3.3: Approximate emissions-based radiative forcing for major species, per the fifth IPCC assessment [7]. Omitted from this figure is the significant uncertainty associated with each metric, especially for the aerosol precursor species.

$$\text{AGWP}_{CH4} = (1 + f_1 + f_2)A_{CH4} \int_0^H e^{-\frac{t}{\tau}} dt = (1 + f_1 + f_2)A_{CH4}\tau(1 - e^{-\frac{H}{\tau}}), \qquad (3.6)$$

where $\tau \approx 12.4$ years is the perturbation lifetime of methane, and $f_1 = 0.5$ and $f_2 = 0.15$ account for the indirect effects on ozone and stratospheric water vapor, respectively; the radiative efficiency, A_{CH4}, equals 3.36×10^{-4} W m^{-2} ppb^{-1}, or 1.2767×10^{-13} W m^{-2} kg^{-1} [7]. For fossil methane, new CO_2 from CH_4 oxidation must also be tracked. Methane GWP$_{100}$ estimates have steadily increased across IPCC assessments, from 21 initially, to 25 in the fourth assessment, and now 28/30 and 34/36 for biogenic/fossil methane with and without climate carbon feedbacks, respectively. Furthermore, these estimates do not include indirect aerosol effects, and their inclusion could further increase GWP values, especially in the short-term (i.e. 20 years) [24]. These progressive updates also complicate somewhat our assessment of most earlier literature, which tends to use smaller GWP$_{CH4}$ values, and when I feel it is especially appropriate, I adjust earlier GWP estimates.

Methane is mainly removed from the atmosphere via oxidation by the hydroxyl radical, and knowledge of this sink constrains global emissions to around 550 TgCH$_4$/year [95], but there is great uncertainty as to the exact origin of methane emissions, both on a national and sectorial basis. In the US, CH_4 emissions are due primarily to, in descending order of importance [25, 95, 10]: (1) livestock, via enteric fermentation and manure management (with enteric fermentation accounting for perhaps 75% of livestock CH_4, based on the EPA inventory [10]), (2) oil and natural gas exploration, with fugitive emissions from natural gas extraction by far dominant, (3) landfills (due to anaerobic breakdown of organic wastes), (4) coal mining emissions, and (5) a variety of minor sources, including wastewater treatment, rice cultivation, abandoned mines, combustion, and wildfires (wastewater is often lumped with the landfill category in top-down estimates). While the EPA's bottom-up inventory of CH_4 emissions has remained quite stable over the last decade, multiple top-down estimates suggest much higher and recently increasing emissions, especially due to increasing natural gas extraction over the southern-central US, and

I discuss this further in the context of unconventional natural gas extraction ("fracking") in Section 4.6.

Several recent studies based on satellite observations have shown very high and increasing methane emissions concentrated over the central and south-central US [95, 96], areas of both large-scale agriculture and livestock production, and oil and gas exploration, and Turner et al. [95] estimated US emissions to be about 50% higher than those tabulated in the EPA's bottom-up inventory.

3.4.3 Nitrous oxide (N_2O)

Nitrous oxide follows CO_2, CH_4, and, as discussed below, the halocarbons, in importance as a radiative forcer. Although halocarbons exert a stronger warming effect, they are being phased out under the Montreal Protocol, while N_2O is increasing in importance with increased global nitrogen fertilizer use and expanding livestock systems. As one might infer, N_2O is primarily associated with agricultural activity and anthropogenic alteration of the global nitrogen cycle, as discussed extensively in Section 20.1.3. Also noteworthy is that, with the phase-out of the ozone-depleting Montreal gases (discussed next), N_2O may become the major ozone-depleting substance. Nitrous oxide is relatively long-lived, with a lifetime of 121 years, and a 100-yr GWP of 298 (which actually slightly exceeds the 20-yr GWP of 268) [7].

3.4.4 The Montreal gases, halocarbons, and other fluorinated gases

Commercially useful halocarbons, broadly divided into *chloro*fluorocarbons (CFCs), *hydrochloro*-fluorocarbons (HCFCs), and *hydro*fluorocarbons (HFCs), have been widely used in aerosol propellants, foam products (e.g. styrofoam), fire retardants, and as industrial solvents, but they are mainly used as refrigerants (i.e. the working fluid for heat exchange in air conditioners and refrigerators). Halocarbons are not only potent GHGs that, as a class, are the third most important well-mixed GHG after methane [7], but those containing chlorine—CFCs and HCFCs, but *not* HFCs—are also powerful ozone depleting substances (ODS), a fact whose discovery led to, by far, the most successful international environmental treaty in history, the Montreal Protocol. Not only has this treaty stabilized the ozone hole, but it has (essentially incidentally) done far more than any other treaty to mitigate climate change [26].

Background for the Montreal Protocol and ozone depletion

In 1974, Molina and Rowland [27] determined that halogenated hydrocarbons containing chlorine (specifically CF_2Cl_2 and $CFCl_3$, better known as CFC-12 or Freon-12, and CFC-11 or Freon-11, respectively) could lead to stratospheric ozone depletion: these molecules are insoluble and inert within the lower atmosphere, thus allowing them to diffuse into the stratosphere where they persist for 50–100 years [7], and where UV radiation causes photolytic dissociation of the chlorine atom; free chlorine in turn catalytically destroys ozone (in a two-step reaction):

$$CF_xCl_y \xrightarrow{h\nu} CF_xCl_{y-1} + Cl, \tag{3.7}$$

$$Cl + O_3 + O \rightarrow Cl + 2O_2. \tag{3.8}$$
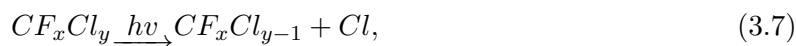
Further work confirmed the ozone threat, and the US, Canada, and several other countries banned the use of CFCs in aerosols (but not other uses) in the late 1970's, but many European countries opposed significant limits on CFCs [30]. Consumers also voluntarily reduced use of CFC-containing products, arresting the previously rapid growth in CFC consumption, and even leading to a transient decrease in CFC emissions [32].

Despite CFC stabilization resulting from the "1974 warning," CFC production began to tick up in the later 1980's with increased demand [30, 32]. Given that early models predicted the overall ozone-depleting effect of CFCs to be relatively small [28], concern over CFCs waned [28] and there was little further action until, in 1985, Farman and colleagues [31] published data revealing the existence of dramatic and worsening seasonal ozone depletion occurring above Antarctica, with October ozone levels about 30% lower than during previous decades, a completely unexpected phenomenon [28, 29] that turned out to be a consequence of chemical reactions in polar stratospheric clouds (PSCs) that liberate chlorine from chemical "reservoirs," and global meteorological patterns.

Briefly, the global atmospheric circulation moves chlorine to the Antarctic atmosphere. In the Antarctic winter (spring in the Northern Hemisphere), the Antarctic Vortex isolates the regional atmosphere such that, in the absence of sunlight and fresh warm air, the stratosphere drops to a bitterly cold -80 to -90 °C, in turn causing PSCs to form. Chemical reactions on the PSCs liberate chlorine from reservoirs such as HCl, and the chlorine then catalytically destroys ozone via several novel reactions [28, 29].

The striking demonstration of a large and growing ozone "hole" helped galvanize support for serious international political action, via the Vienna Convention of 1985 and then the Montreal Protocol, ratified in 1987, just 13 years after Molina and Rowland's seminal work and in the face of significant scientific uncertainty and industry opposition [30]. The Montreal Protocol imposed emissions limits and a gradual phaseout first of CFCs and then HCFCs (HCFCs were initially developed as CFC replacements with a lower, but non-zero, ozone-depleting potential). Limits were strengthened and the phaseout schedule accelerated over eight subsequent revisions to the protocol. Complete CFC phaseout was completed in 2010, while the less potent HCFCs, which are still widely used for refrigeration/air conditioning in developing countries and to a lesser extent in the West, are to be eliminated by 2030 [26].

In the absence of the Montreal Protocol, CFC emissions almost certainly would have continued to increase from the 1970's to cause eventual widespread global ozone depletion [29], along with severely exacerbated global warming. Instead, atmospheric chlorine concentrations are slowly decreasing and stratospheric ozone appears to be recovering, although long CFC lifetimes mean that these chemicals will continue to affect the atmosphere for many years.

Global warming and Montreal

All halocarbons are potent GHGs, and the IPCC [7] estimated that, as a class, these gases exerted a direct RF of 0.36 W m^{-2} in 2011, with CFC-12 and CFC-11 accounting for about two-thirds of this forcing; CFC-113 and HCFC-22 account for most of the rest. Note that this is despite CFC production being fully phased out and relates to the long lifetimes and very large radiative efficiencies of these substances. Subdividing, the Montreal gases (i.e. CFCs and HCFCs) have a direct RF of 0.33 W m^{-2}. However, ozone is also a strong GHG and so its depletion has a global cooling effect; this RF estimate adjusts downward to 0.18 W m^{-2} after accounting for the loss of ozone. The HFCs have an RF of 0.02 W m^{-2} (dominated by HFC-134a which is the principle refrigerant for mobile/automotive air conditioners), while other fluorinated gases add 0.01 W m^{-2}.

On the whole, the Montreal Protocol has been a boon for the climate: the direct RF from Montreal gases was 0.32 W m^{-2} in 2000 and has remained essentially stable since, but would likely have reached 0.60–0.65 W m^{-2} by 2010 without intervention [26]. Even accounting for the indirect cooling effect of ozone depletion (30–45% RF offset), this would have meant a 7–9% higher total anthropogenic RF in 2011. Even more dramatically, a 2007 work by Velders et al. [32] estimated that, had the 1987 Montreal Protocol not been put into place, in terms of GWP, ODS emissions could have reached 15–18 GtCO$_2$e/yr (equivalent to about half of

44

CO$_2$ emissions), while had the 1974 "early warning" not occurred, ODS may have reached a staggering 24–76 GtCO$_2$e/yr (comparable to or even worse than CO$_2$ emissions); see also Figure 3.4 below. After adjusting for the cooling effect of ozone depletion, the Montreal Protocol still prevented emissions on the order of 10 GtCO$_2$e/yr in 2010, or about 20% of all anthropogenic GHG emissions in that year [26]. Instead of these dire numbers, carbon equivalent halocarbon emissions were about 1 GtCO$_2$e in 2011 [7].

Now, despite the clear climate benefits of Montreal, it has had one major weakness with respect to climate: HFCs (which again, lacking chlorine do not deplete ozone) used as CFC/HCFC replacements are also strong GHGs. The current mix of HFCs has an average atmospheric lifetime of 15 years and a GWP of 1600 [26], but low-GWP alternatives are available and in use. These alternatives include very short-lived HFCs, hydrocarbons such as propane, and CO$_2$. Without action on HFCs, given their rapid recent growth, HFC radiative forcing could increase from 0.012 W m^{-2} in 2010 to as much as 0.4 W m^{-2} in 2050 (or about 20% the current CO$_2$ RF) [34].

Fortunately, an amendment was very recently adopted (October 15, 2016) to largely phase HFCs out by 2050, under the Montreal Protocol. The plan has developed countries reducing HFC use beginning in 2019 with an 85% reduction by 2036, while most developing countries will reduce consumption 80% by 2045 [33]. This phaseout has the potential to avoid up to 0.5 °C of warming by 2100 and 80 billion tonnes CO$_2$e [33, 34].

Current halocarbons and use

HFC-134a is widely used in mobile (automotive) air conditioners (MACs), and it is the most important HFC. It is an unfortunate feature of these ACs that they leak slightly during operation, and it is eventually necessary to recharge the refrigerant, a process that itself can result in significant HFC-134a venting (especially for DIYers). For a typical passenger vehicle in the US, leak rates are on the order of 50–100 g/yr for older models [36], but this rate is trending down, with more recent model years leaking from <10 to about 25 g/yr [35]. Therefore, a typical driver adds anywhere from 16 to 156 kgCO$_2$e (at an HFC-134a GWP of 1550) from their onboard AC. While nontrivial in the aggregate, this is but a fraction of the CO$_2$e emissions resulting from the fuel used to power MACs (up to 10% of all automotive fuel, as discussed in Section 7.1.2), and less than 2% of all passenger vehicle CO$_2$e emissions. Note that summer HFC-134a emissions are two to three times those in winter [37], a fact largely attributable to higher use and service rates in summer (hence, further motivation to avoid unnecessary AC use).

A lesson for climate change?

It is clear that robust international cooperation was necessary to avoid catastrophic CFC emissions, a situation analogous to that of carbon today. There is, perhaps, a lesson to be learned from the two stages of the CFC phaseout. That is, following the 1974 warning, CFC emissions halted their rapid increase as a result of limited government restrictions (isolated to individual nations) and changing *consumer* behavior and demand. It took a high-level international treaty 13 years later, along with new technologies, i.e. HCFCs and HFCs with lowered or zero ozone-depleting potential, to definitively address the crisis. It is also unlikely that, without a willing and aware population, international action could have been effected.

I believe the carbon situation is somewhat similar to the 1974-1987 interim today: climate change is a global problem that will require international cooperation *and* alternative technologies (widespread renewable energy, etc.) to definitively solve. However, conservation measures, relatively isolated political actions (i.e. at the community, city, state, or national, but not international, scale), and an informed consumer class that takes emissions reductions seriously *can*
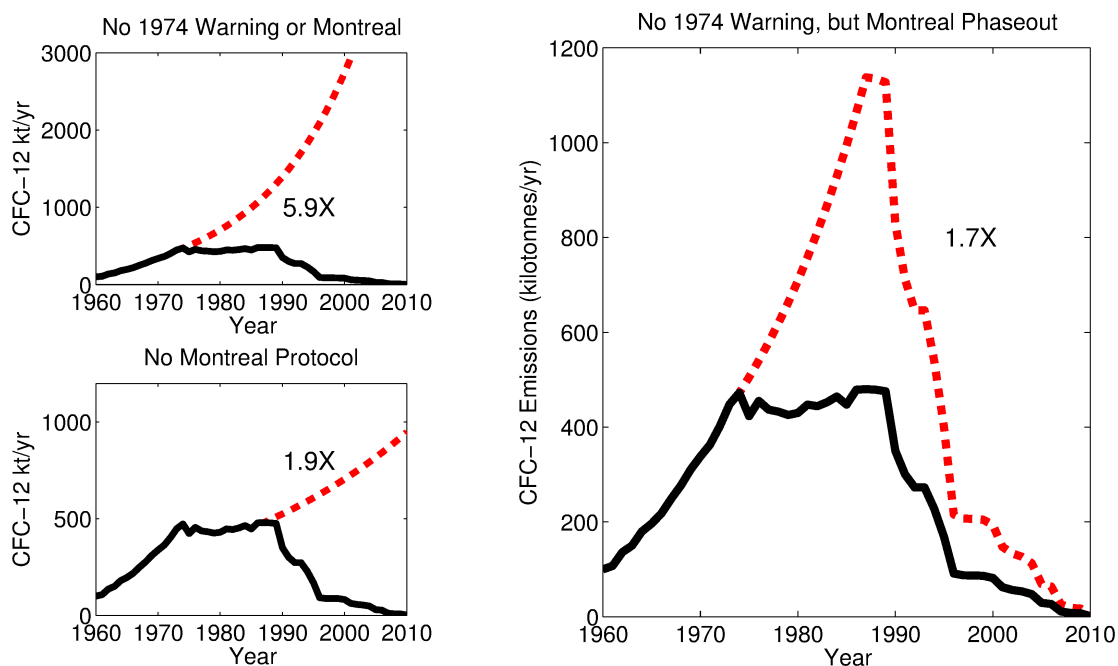
Figure 3.4: The left two panels show hypothetical CFC-12 emissions scenarios: (1) 7% annual growth in CFC production/emissions from 1974 onwards without the 1974 warning or Montreal Protocol, or (2) the 1974 warning but without the 1987 Montreal Protocol, leading to 3% annual CFC growth subsequent to 1987. The black line shows the actual CFC-12 production (the CFC-11 curve is similar); inset numbers show hypothetical cumulative emissions from 1960 to 2010 relative to truth. On the right, we have a third scenario: no consumer/national response to the 1974 warning, but definitive phaseout via international action in 1987. Although disaster is ultimately averted, cumulative CFC-12 emissions are 70% higher, and 100% higher between 1974 and 2010.

reduce CO_2 emissions, even without broader political action or technology change.

By checking carbon emissions until definite phase-out of the carbon economy, we can dramatically lower the overall burden on the climate system. To see this by way of comparison, suppose, as a thought experiment, that CFC emissions had continued unabated after 1974 (ODS emissions were likely to have continued growing by at least 7% annually without the 1974 warning [32]), but that the Montreal Protocol of 1987 yielded a comparable phaseout (but of course, from higher baseline CFC emissions). In this case, cumulative CFC-12 and CFC-11 emissions would have been almost 70% higher before complete phase-out in 2010 (and clearly a full phaseout by 2010 would have been less likely, with more infrastructure and political capital committed to CFCs). Looking at just 1974 on, cumulative emissions would have doubled without the 1974 consumer response. Thus, in a crude sense, consumer behavior accounted for about 50% of the avoided CFC emissions from 1974 through 2010. This, and alternative worlds where either the 1974 warning or Montreal protocol did not exist (adapted from [32]), are illustrated in Figure 3.4 for CFC-12.

Of course, fossil fuels are fundamental to industrial civilization in a way that CFCs never were, and one may challenge my analogy on such grounds, but the hard fact remains that fossil fuels *must* be phased out sooner or later, either via geologic or political constraints, and so, I think, the basic lesson of the CFCs still holds.

3.4.5   Aerosols

Sulfate

Sulfate (SO_4) aerosols are the major anthropogenic cooling aerosols, with the AR5 estimating a global radiative forcing of -0.40 W m^{-2} (-0.60 to -0.20) in 2011 due to these substances, which are primarily formed from sulfur dioxide (SO_2) emitted by fossil fuel burning, especially coal-fired power plants and fuel oils. To derive GWP values for SO_2, we first have that some fraction of an SO_2 pulse emission evolves to SO_4 (sulfate), which persists in the atmosphere for about 4 days and causes cooling by directly reflecting solar radiation. Now, by dividing the steady-state sulfate forcing by annual SO_2 emissions, we get an equivalent instantaneous RF for SO_2, estimated at -3.2×10^{-10} W m^{-2} kg^{-1} by [39]. Multiplying by the lifetime of 4 days, we get the total time-integrated radiative forcing from SO_2, and we then divide by the time-integrated forcing of a CO_2 bolus at any time. Via this process, Fuglestvedt et al. [39] derived GWP_{20} and GWP_{100} values of -140 and -40, respectively, for the direct radiation scattering effect of SO_2 emissions; several other similar estimates are also summarized in this work.

Sulfate aerosols also alter cloud structure for a further cooling effect, and including these indirect effects in our GWP estimates may increase their magnitude greatly, with Lauer et al. giving several 100-yr GWP estimates roughly ten times those above, for SO_2 emissions from shipping; Shindell et al. [24] somewhat similarly estimated GWPs about twice those above (GWP_{20} -268, GWP_{100} -76), but the uncertainty in these indirect effects is extreme.

Increased controls have reduced SO_2 emissions in the developed world, e.g. from scrubbers installed at coal power plants and the adoption of ultra-low sulfur diesel fuel. While valuable for improving local and regional air quality, absent concomitant CO_2 reductions, these controls can increase warming, and represent, to some degree, environmental problem shifting.

NO_x

Nitrogen oxides (NO, NO_2, and NO_3^-, collectively labelled NO_x) have competing warming and cooling effects that act over different timescales, and the balance depends strongly on the altitude of emissions, latitude, and local atmospheric conditions. In the troposphere (lower atmosphere), NO_x emissions catalyze the oxidation of CH_4 and other VOCs to form ozone (O_3) by the hydroxyl radical (OH), increase levels of OH and thus decrease the lifetime of CH_4, and form nitrate aerosols that reflect solar radiation [7]. That is, somewhat confusingly, NO_x has two separate effects on methane: (1) oxidation leading to methane destruction (cooling) and ozone formation (warming), and (2) decreased methane lifetime (cooling). Ozone has a strong, but very short-lived warming effect, as tropospheric ozone has a mean lifetime of 22.3 days [38], while the decrease in average methane lifetime has a longer-lived cooling effect. In general, NO_x has a long-term overall negative radiative forcing, i.e. 'tis cooling.

Note that NO_x emissions can also enter into the global nitrogen cycle (see Section 20.1.2) by depositing onto soils, increase plant CO_2 uptake via nitrogen fertilization, and evolve to N_2O with associated warming (see Figure 20.2 of Section 20.1.2), and these second-order influences are poorly quantified.

NO_x emissions may be divided by source into aviation, surface, and shipping NO_x. Shipping NO_x has a strong cooling effect over all time-horizons, with net GWP_{20} between -76 and -31 (mid-estimate -47), and GWP_{100} -36 to -25 (mid-estimate -32, and GWPs per kg N), based on several studies compiled by [39], and considering the effects of NO_x on ozone formation, ozone-related methane destruction, and methane lifetime.

Aviation NO_x, on the other hand, likely has net warming effects, at least in the near-term, as NO_x efficiently creates ozone at high altitude, and the warming effect of ozone is greater

at altitude [263]; 100-GWP estimates for aviation NO_x range from -2.1 to +71 [39], and such emissions are discussed in further detail in Section 8.3.1.

3.4.6 Black carbon

Black carbon (BC), or soot, is a particulate product of combustion of some fossil fuels and biomass that has been increasingly recognized as an important near-term driver of climate change. Chemically, BC is an insoluble aggregate of small carbon spherules that are chemically inert, and it is lost from the atmosphere either by physically settling to the earth's surface or removed via precipitation ("dry" or "wet deposition"). The defining characteristic of BC is its strong absorption of light throughout the visible spectrum: it is quite literally black, and this broad spectrum absorbance translates into a massive heat gain compared to typical greenhouse gases. In addition to absorbing solar radiation, BC affects climate forcing by altering clouds and enhancing the melting of ice and snow upon which it settles. Significant uncertainty surrounds BC in the scientific literature, but I refer the motivated reader to a recent exhaustive (but relatively reader-friendly) review by Bond et al. [41].

Black carbon generally persists in the atmosphere for only a few days to a few weeks, and thus a pulse of BC exerts an extremely powerful but very brief (i.e. days) warming force, in great contrast to the long-lived CO_2. Unlike the well-mixed greenhouses gases, BC exerts its warming effects primarily at a local/regional scale, near the source of emissions. Additionally, BC aerosols have multiple indirect warming and cooling effects, mainly via interaction with clouds that may either increase or decrease cloud cover and through alteration of the regional hydrologic cycle. Black carbon deposited on snow and ice also increases the absorption of solar radiation to increase melting.

Broadly speaking, black carbon is emitted from a few major sources [41]: (1) diesel engines, (2) industrial fossil fuels, (3) residential solid fuels, e.g. wood or dried dung, and (4) "open biomass burning," i.e. open burning of forests, savannahs, and agricultural waste. Because various organic and sulfur-containing co-emissions that result from uncontrolled open biomass burning have a cooling effect on the climate, the net effect of open biomass burning is likely actually climactic cooling. Indeed, taken together, the net climate effect of aerosols from all black carbon-rich sources may be a cooling one. On the other hand, BC from diesel combustion and residential fuel use almost certainly has a strong warming effect, and these two areas represent attractive mitigation targets [41].

Global emissions and radiative forcing

As reviewed in AR4, estimates of global BC emissions vary between about 5.8 to 8.0 Tg BC [9]; recently Bond and colleagues [41] estimated global emissions of 7.5 Tg BC for the year 2000 from a bottom-up inventory, but the uncertainty of this estimate is great.

Several global-scale estimates of the radiative forcing attributable to BC implicate it as the second- or third-most important contributor to anthropogenic climate change. The most recent IPCC assessment (AR5) estimated the overall direct radiative forcing of aerosol black carbon (BC) to be 0.40 (0.05 to 0.80) W m^{-2}, a doubling over the prior IPCC estimate (point estimate 0.20 with the range 0.05 to 0.35 in AR4). Black carbon deposited on ice and snow was considered an additional minor contributor at 0.04 W m^{-2} (a reduction from the AR4 estimate).

Direct radiative forcing and GWP

While its indirect effects and disparities in time- and spatial-scales relative to CO_2 have led some authors to criticize application of the GWP framework to BC [42], there do exist several

published estimates of a GWP for BC, and indeed, the mathematical description of the *direct* radiative forcing of BC is quite straightforward, mimicking that of short-lived greenhouse gases.

Bond and Sun [43] estimated 100-yr and 20-yr GWPs of 680 (210–1500) and 2200 (690–4700), respectively. They assumed a simple exponential decay pattern for BC, and compiled several estimates for BC atmospheric lifetime which ranged from 2.4 to 8.4 days. Point estimates from seven modeling studies ranged from 4.4 to 7.3 days, with a mean of 5.5 days (or 0.0151 years), which was taken to be the exponential decay factor. Their median estimate for radiative efficiency was 1800 W/g (range 900–3200), which converts to 3.5287×10^{-9} W m^{-2} kg^{-1}, assuming a global surface area of 510.1 trillion m^2. This is about 2 million times the radiative efficiency of CO_2. Given the very brief atmospheric residence time, we can simply assume that all heat energy is deposited instantaneously, and we have the absolute GWP of some quantity of BC as:

$$\text{AGWP}_{\text{BC}} = A\tau R \approx A(5.3172 \times 10^{-11}) \tag{3.9}$$

where A is BC mass (in kg), τ is the mean lifetime (in years), R is the radiative efficiency given above, and the approximation assumes $\tau = 5.5$ days.

3.5 Carbon stocks and sinks

3.5.1 Soils

The soil is the largest terrestrial carbon store, and therefore human activities that perturb soil may have a profound influence on global warming. Indeed, Jobbgy and Jackson [44] estimated global soil stores, within the top three meters of soil, at 2,344 GtC, about five times the remaining human carbon budget. While from the year 2000, this figure is still widely cited, and represents a large increase from prior surveys which had typically counted carbon only in the first meter of soil. It follows that even small relative changes in this store are globally significant. There is much that is unknown about the dynamics of soil organic carbon (SOC), and how both human activities and natural events, such as fire, influence this carbon pool.

All SOC is ultimately derived from the breakdown of plant matter. As plant matter decomposes, the carbon is oxidized to CO_2 to generate energy by microbes and myriad other detrivores, such as worms. While most carbon is consumed relatively quickly for energy, some persists for many hundreds to thousands of years. On the most basic level, the quantity of SOC is determined by balance between the input from plant matter production and output due to decomposition. Environmental factors influence both these rates. On the regional scale, precipitation and temperature are the primary arbiters of this balance. As temperature goes up, plant productivity and decomposition both increase, but based on global surveys, the balance tends to favor decomposition, and SOC falls. Thus, large amounts of SOC are stored in the great northern boreal and arctic ecosystems [45].

The concentration of SOC is greatest closest to the soil surface, and steadily declines with depth. However, more carbon overall is stored in the deep soil than in the topsoil. As one goes down in depth, the rate of decomposition decreases, and thus the age of the carbon pool increases. Carbon in the subsoil is ancient, and may persist for many thousands of years.

Agriculture is the major human activity that perturbs soil carbon stores, and it is very consistently found that conversion of native ecosystems, such as prairie or forest, to crop or pasture results in marked soil carbon losses. As elaborated further in Section 20.3.1, the conversion of US prairies to arable crops (e.g. grains) may result in >50% soil organic carbon losses in the upper soil layers [379, 381].

Overgrazing is the leading worldwide cause of desertification, and, like conversion to cropping, can lead to marked soil carbon losses [405, 389]. It is possible that well-managed grazing systems under *light* grazing pressure, in parts of the Great Plains region of the US, can modestly increase SOC stores, but, as discussed extensively in Section 21.2.2, the weight of the evidence suggests little overall effect except when overgrazing severely degrades the land, and on balance grazing has almost certainly been harmful to both US and global soils.

Forest soils are also vulnerable to agriculture: Conversion of tropical forest to tree plantations of cash-crops (such as oil palm, rubber, and cacao) results in massive carbon losses in *above*-ground carbon stocks, but also leads to very appreciable soil organic carbon loss. Tropical forest soils store an estimated 692 billion Mg of carbon in the top three meters (roughly 10 feet) [44], and even small perturbations in this carbon pool from land-use change can translate into large atmospheric fluxes. Multiple mechanisms contribute to soil carbon loss. Land conversion dramatically increases soil erosion due to the loss of protective ground cover. With the loss of forest litter, a constant carbon input to the soil is lost. Without replenishment, the labile soil carbon pool is lost, and the deeper carbon pools may suffer ongoing decomposition without new inputs [48]. The loss of vegetative cover also increases soil temperature, which in turn increases carbon loss, and the trampling of soil alters its mechanical properties [49].

3.5.2   Forests

Worldwide, forests are a major carbon sink, and it has been found that even undisturbed old-growth forests have been absorbing large amounts of carbon over the last 50 years [46]. This is driven at least in part by global increases in atmospheric carbon dioxide and reactive nitrogen from fossil fuel burning and fertilizer manufacture, but also likely by historical land-use changes. While the worldwide transition to fossil fuels as civilization's principal energy sources over the last century and a half has largely fueled climate change, this transition did dramatically reduce the use of forest biomass for energy (and for other agricultural uses), allowing the forests of America and Europe, degraded from vast over-harvesting, to begin recovering, and in this ongoing recovery, to sequester large amounts of carbon [47].

The finding that old-growth forests are rapidly absorbing carbon undercuts a major rationale for biofuel use, i.e. that it is carbon-neutral, as this implies that not only must a harvested forest regrow to its prior state before the carbon-debt can be considered paid, but we must account for the additional growth that would have occurred in the absence of a harvest, and such dynamics are discussed in far more detail in Section 3.8.

While forest growth (and regrowth) is a carbon sink, deforestation, primarily in the tropics, is a major carbon source [46]. There is significant uncertainty concerning the sizes of both the global and tropical carbon sink from regrowth and source from deforestation. What is clear is that carbon losses, on a per-area basis, are truly massive when tropical forest is cleared for crops or pasture [70] (most often to support beef production).

Finally, the US EPA inventory provides detailed estimates on US forest area and carbon stocks, divided into above- and below-ground biomass, dead wood, litter, and soil organic carbon. This inventory is in rough agreement with a similar accounting by Smith et al. [617], and, overall, US forests store about 100 MgC per hectare (Ha, equal to 10,000 m^2, or 2.47 acres) in above-ground biomass.

3.5.3   The Seas

I note here that the ocean is the most significant sink of anthropogenic carbon, having absorbed 41% of all humanity's carbon emissions from fossil fuels and cement [71], also resulting in gradual acidification of the ocean, with deleterious effects on sea life. Furthermore, the ocean is, by far,

the greatest sink of the Earth's excess heating due to warming emissions, with 93% of the excess heat from 1970 to 2011 being stored in the oceans [7].

## 3.6 An introduction to respiration, combustion, and heating values

- Respiration is the cellular conversion of glucose (and other organic hydrocarbon chains) and oxygen (O_2) to CO_2, H_2O, and heat.

- Combustion is a similar reaction involving O_2 and fossil fuel hydrocarbons with the general formula C_xH_y.

- Of fossil fuels, natural gas has the highest hydrogen content, highest energy content (heating value), and lowest CO_2 emitted per kWh of heat released by combustion. Coal has the lowest hydrogen content and highest CO_2 emissions per kWh; petroleum fuels are intermediate.

- Combustion byproducts result from nitrogen in air, sulfur contaminants in fuel, and incomplete combustion.

The cyclical conversion of energy, H_2O, and CO_2 to energy-storing carbohydrates and O_2, and visa versa, is the energetic basis for almost all life on earth, with photosynthesis representing the energy storage pathway, and respiration the energy-releasing pathway:

$$6CO_2 + 6H_2O \xrightleftharpoons[\text{Respiration}]{\text{Photosynthesis}} C_6H_{12}O_6 + 6O_2. \tag{3.10}$$
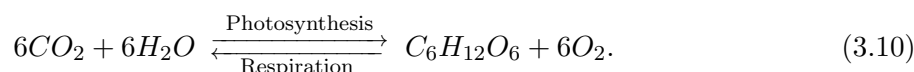
Downstream of photosynthesis, glucose, $C_6H_{12}O_6$, can be converted to a variety of other biological molecules that act to store energy, such as lipids (long-chain hydrocarbons), or have a structural role, such as cellulose (these structural molecules still store useful energy that may be released upon digestion or burning). The carbon-based products of photosynthesis have provided almost all the energy powering human civilization, either as fresh biomass or ancient fossil fuels. Biological molecules and fossil fuels are extremely similar energy sources: both are based on carbon chains, and the latter result from anoxic breakdown of organic matter under high heat and pressure. Respiration is an oxidation reaction that is essentially a "slow burn," with products identical to those produced when glucose is combusted.

Combustion, an exothermic reaction between a fuel and an oxidant to yield heat and oxidized products, is similar to a fast version of respiration when a hydrocarbon fuel, with the general formula C_xH_y, interacts with O_2 to yield H_2O, CO_2, and heat:

$$C_xH_y + \left(x + \frac{y}{4}\right) \rightarrow xCO_2 + \frac{y}{2}H_2O + \text{Heat}. \tag{3.11}$$
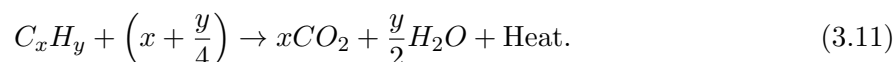
We can calculate the energy released in any particular reaction using the *enthalpy of formation*, H_f, defined as the enthalpy (or heat) change resulting when a compound is produced from its elements in their standard state. Typically, H_f is negative, indicating that heat is released, and the overall enthalpy of a reaction is the difference between H_f for the reactants and products. For example, for the combustion of methane, CH_4, we have

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \tag{3.12}$$

and our enthalpies of formation, under standard conditions (1 atm pressure, 298.15 K), are $H_{f(CH_4)}$ = -74.9 kJ/mole, $H_{f(CO_2)}$ = -393.5 kJ/mole, $H_{f(H_2O(l))}$ = -285.8 kJ/mole, and $H_{f(O_2)}$

= 0 kJ/mole [54]. Thus, the (product - reactant) difference is -890.309 kJ/mole, equal to -15.42 kWh/kg (this is the higher heating value, explained below). From the stoichiometry of Equation (3.12), we have that each kg of CH_4 yields (44.01/16.04) kg of CO_2, and, therefore, we can derive an emissions factor of 0.178 kgCO_2/kWh. That is, for every kWh of (gross) heat energy released by CH_4 combustion, we also get 0.178 kgCO_2.

At this point we must distinguish between the *higher heating value* (HHV) and the *lower heating value* (LHV). Water is a major combustion product, and at high temperature is formed as vapor, not liquid. Since water has a very high heat of evaporation, a significant fraction of the reaction energy is locked into water vapor as latent heat. This heat can only be usefully recovered if the water condenses to a liquid, but it is usually lost as part of the flue gas. For example, water vapor generated in internal combustion engines is invariably lost with the tailpipe exhaust, while advanced condensing furnaces can recover this latent heat. The HHV (or "gross energy") is defined as the heat released by a reaction occurring at 298 K (24.85 °C), with the reaction products returned to 298 K, and thus includes the latent heat in water vapor, and we use the enthalpy of formation for liquid water, as above. The LHV (or "net energy"), on the other hand, is the heat released when reactants return to 150 °C, and thus we lose the latent heat in water vapor, and it is appropriate to use the enthalpy of formation for water vapor [54]. We can repeat the calculation above to get the LHV by using the enthalpy of formation for water vapor, $H_{f(H_2O(v))}$ = -241.8 kJ/mole, giving us net energy of -802.3 kJ/mole, or -13.89 kWh/kg.

While HHV, or gross energy, may be more commonly used, LHV is also in widespread use, especially for transportation fuels, and there can be significant confusion when sources do not clarify. Using the LHV can inflate efficiency measures, and the HHV is generally the most appropriate for overall efficiency calculations.

Different fuels, obviously, have different energy (heat) contents, but more importantly, the amount of CO_2 per kWh of energy also varies significantly between fossil fuels, with coal the worst performer (at the point of combustion, woody biomass actually releases even more CO_2 per kWh than coal, as discussed in Section 4.10.1), and natural gas (methane) the best. Generally speaking, the more hydrogen by mass in a carbon-based fuel, the higher the energy-density, and the lower the CO_2 per kWh [51, 54], explaining why methane, with its four hydrogen atoms to a single carbon, is the cleanest-burning hydrocarbon. For an *n*-alkane, our general combustion reaction is

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O + \text{heat}, \tag{3.13}$$
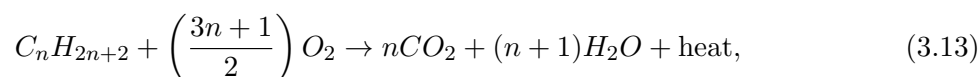
and the enthalpy of formation for the *n*-alkane increases in absolute value by almost exactly 5 kcal/mole (20.92 kJ/mole) with every additional CH_2 group, from -20 kcal/mole for ethane, C_2H_6 [53]. From this relation, and the enthalpies of formation above, we can compare the combustion characteristics of liquid/gaseous fossil fuels as in Figure 3.5. As seen, the lighter short-chain hydrocarbons are higher in energy (on a mass-basis), and release less CO_2 per kWh of energy generated. Since long-chain hydrocarbon mixtures are denser, on a volumetric-basis these fuels (e.g. diesel and fuel oil) are more energy dense, a factor salient, for example, when comparing miles per gallon achieved by diesel and gasoline vehicles.

Coal, unlike natural gas and petroleum-based fuels, is highly heterogeneous, and is composed of a mixture of non-combustible minerals (ash), water, and complex carbon chains with hydrogen and oxygen [54]. Coal also tends to contain 1–2% sulfur. Coals containing more hydrogen by mass emit somewhat less CO_2 per kWh [51], but all have a high CO_2/kWh ratio, as seen in Figure 3.5.
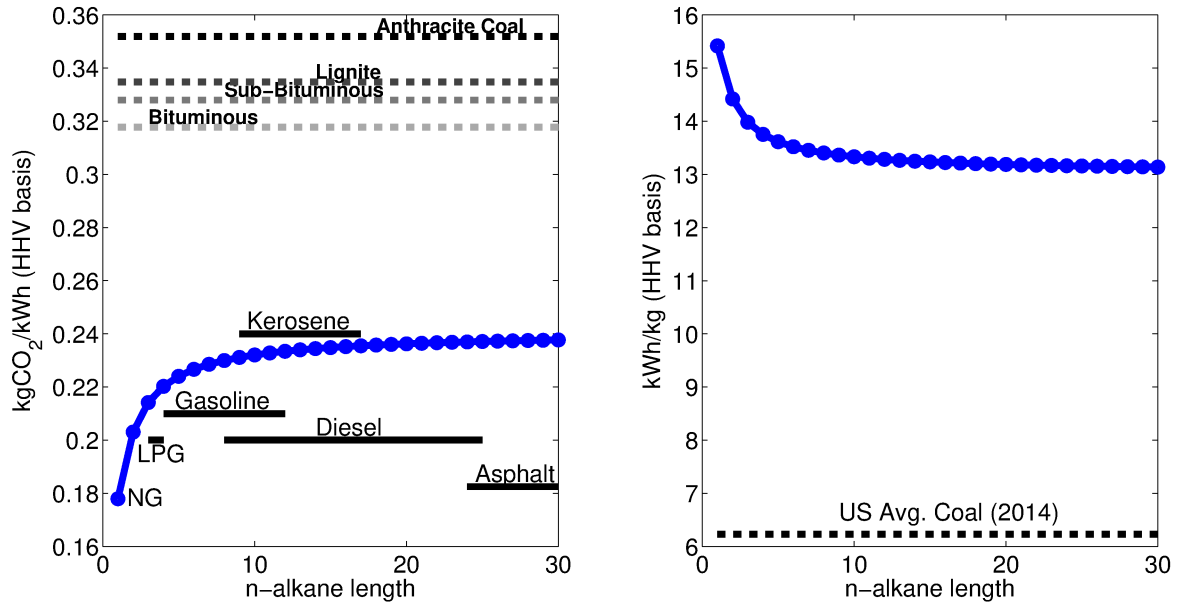
Figure 3.5: Theoretical emissions factors and energy-densities for alkanes of various lengths, on a HHV-basis. The left panel gives $kgCO_2/kWh$ at the point of combustion for n-alkanes, along with this metric for different ranks of coal (per [51]). Approximate chain-lengths for common petroleum fuels are demonstrated. The right gives theoretical energy-density on a mass-basis, along with US average coal heat content in 2014 [114].

3.6.1 By-products of combustion

Fossil fuel combustion has several by-products, mainly sulfur oxides and nitrogen oxides, with incomplete combustion also yielding carbon monoxide and soot (black carbon). Coals are generally 0.5–5% sulfur by weight [54], crude oils average about 1.5% sulfur [207], while natural gas usually contains only scant amounts [55]). Oxidation of fuel sulfur leads to sulfur dioxide (SO_2), which ages to SO_4 and causes regional air pollution and cooling effects (see Section 3.4.5).

Nitrogen oxides (NO_x) are not related to any contamination, but a product of oxidized nitrogen (N_2) that naturally makes up 79% of the air. Hotter combustion conditions, which lead in general to more efficient engine operation and more complete combustion, are also more likely to yield NO_x. NO_x aerosols have a mix of warming and cooling effects, as detailed in Section 3.4.5. Unoxidized carbon gives soot (a.k.a black carbon, which is strongly warming), while partially oxidized carbon gives carbon monoxide (CO) (also warming). Thus, we have ideal combustion as

$$O_2 + N_2 + C_xH_y + S \rightarrow CO_2 + H_2O + N_2 + S, \tag{3.14}$$
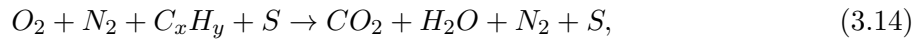
with no oxidation of fuel sulfur or air nitrogen, but actual combustion as

$$O_2 + N_2 + C_xH_y + S \rightarrow CO_2 + H_2O + NO_x + SO_x + CO + C_{\text{soot}}. \tag{3.15}$$
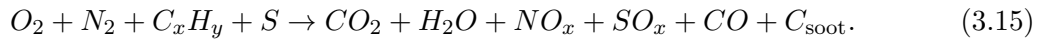
A variety of other particulates, oxidation products, etc., are also released depending upon the fuel and combustion conditions, e.g. mercury in coal, and various organic carbons released from wood burning.

3.7 An introduction to fossil fuels

Three major forms of fossil energy together provide almost all the world's energy: coal, oil (and the derived petroleum fuels), and natural gas. Furthermore, burning these fuels is the major driver of climate change. Here, I provide a brief introduction into the origins, properties, depletion dynamics (e.g. "peak oil"), and general emissions factors for these fuels. These fuels receive further dedicated attention elsewhere: coal and natural gas are discussed in further detail in the context of electricity generation, in Chapter 4, while tar sands oil is covered in the context of transportation fuels, in Chapter 6.

3.7.1 Origins and basic properties

All fossil fuels are formed via the burial of organic matter under multiple layers of inorganic sediments, leading to compression under high pressure and temperature, and the formation of carbon- and hydrogen-rich hydrocarbons. This deep burial and a lack of oxygen prevent the degradation that is the usual fate of dead organisms. Coal is formed when forest matter is buried in low oxygen marshes to form peat, which then transforms into successive grades of denser and denser sedimentary coal rock, as detailed further in Section 4.5; much coal dates from the carboniferous period, when the earth's land was largely covered in marshy tropical forests. Coal has the highest carbon:hydrogen ratio of the fossil fuels, the lowest heating value, and the highest CO_2/kWh emissions (see Figure 3.5).

Oil and gas, on the other hand, are generally formed when microscopic marine life, such as algae and zooplankton, are buried in deep anoxic ocean sediments, often in a deep *basin* [55]. *Conventional* oil and gas reserves form as follows. Organic matter in a *source* rock, often a shale (sedimentary rock made up of fine clay and some organic matter), is transformed by heat/pressure into oil. Between temperatures of about 65 and 150 °C, crude oil is formed (along with small amounts of gas), the so-called oil window, while at greater temperatures natural gas is formed, as shown in Figure 3.6. Now, oil and gas produced in shale expand, and with sufficient pressure the source rock is temporarily fractured, allowing these hydrocarbons to migrate through the subsurface, where they may encounter layers of more porous sedimentary rock.

Sedimentary rocks that are highly porous and permeability allow oil from source rocks to travel relatively freely, and these are referred to as *reservoir* rocks. Now, oft-times on its travels oil will encounter a *trap*, essentially a convexity in the reservoir rock overlain by an impermeable *caprock*, where these hydrocarbons can accumulate. Reservoirs may consist of either solely oil (with some dissolved natural gas, a so-called unsaturated pool); an oil reservoir overlain by natural gas–the free gas cap (a saturated pool); or a pure gas reservoir. Water, usually highly saline brine, is present at depth and occurs at the base of all reservoirs (water is much denser than oil or gas). This process is demonstrated in Figure 3.7.

Crude oils consist of a mix of straight hydrocarbon chains (alkanes), closed hydrocarbon rings (naphthenes), and aromatic hydrocarbon rings. Oils consisting primarily of shorter hydrocarbon chains are light, while longer, dense hydrocarbon mixes are heavy. Depending on its sulfur content, oil is referred to as sweet (low sulfur) or sour (high sulfur), with light, sweet oils the most valuable. All crude oil begins light, but when it seeps to the surface (or near surface), the lighter fractions may be lost to evaporation and water flows, and degraded by bacteria, yielding lower quality heavy oils. The Alberta tar sands are an example of a highly degraded, heavy bituminous oil.

At the refinery, crude oil is separated into fractions via distillation, such that the lightest fractions (composed of the smallest molecules) are gaseous, and include liquid petroleum gas (LPG) and propane, followed by gasoline. Kerosene, which is the basis for jet fuel, is of medium
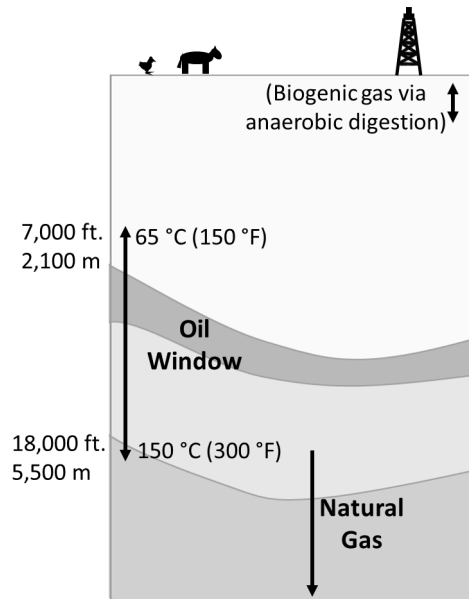
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Figure 3.6: The oil window occurs between 65 and 150 °C, or about 2,100 to 5,500 m in depth on land (7,000 to 18,000 feet). Deeper and hotter, crude oil permanently degrades to graphite and natural gas. Note that natural gas can also be formed near the surface when bacteria anaerobically break down organic matter.

density, while heavier fractions make up diesel and heavy fuel oils, with bitumen/asphalt the densest and heaviest of all, as seen in Figure 3.8. Gasoline is generally the most valuable fraction, and therefore some heavier hydrocarbons are processed to gasoline via *cracking* [55].

Natural gas from the field varies in its exact composition. It is always mostly methane, but small amounts of ethane and nitrogen gas can be present, as may trace amounts of butane, propane, and hydrogen sulfide (a gas with significant sulfur content is a sour gas). Natural gas as delivered to customers is nearly pure methane.

3.7.2 Unconventional oil and gas

- Unconventional oil and gas resources are present in low permeability *tight* formations, either clay source shales or low permeability sandstone reservoirs.
- Hydraulic fracturing and horizontal drilling have markedly increased unconventional oil and gas production in the US since about 2000.

Conventional gas and oil reservoirs, as just discussed, are formed when hydrocarbons from low permeability source rocks, typically clay shales with high organic content, seep into higher permeability reservoir—sandstone or carbonate—rocks. Unconventional oil and gas come from *tight* formations, either sandstones or carbonate formations of low permeability, or the low permeability source shales themselves. By 2015, almost 70% of US natural gas and 50% of US oil came from unconventional sources.

Extraction from tight formations, especially shale, did not become economical until the advent of horizontal drilling techniques and hydraulic fracturing. With horizontal drilling, a single well-bore is drilled horizontally through a formation. Then, fracking fluid, a mixture of
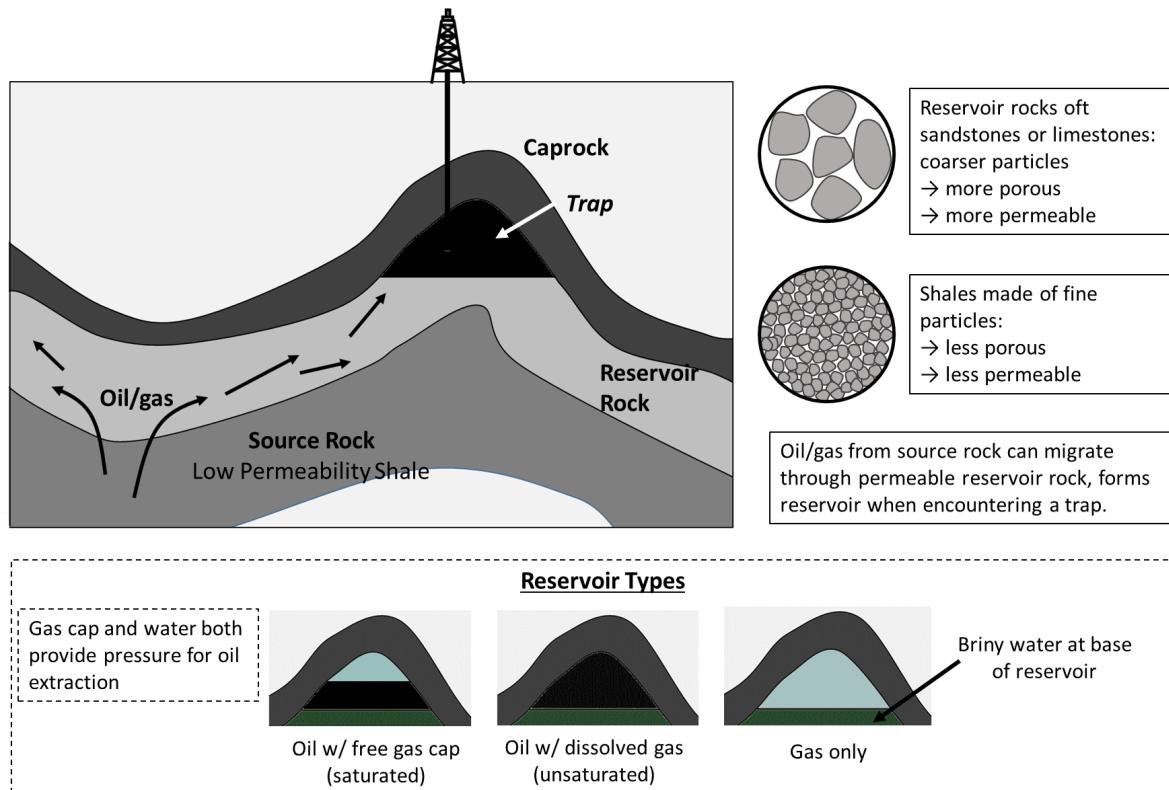
Figure 3.7: Schematic for the formation of conventional oil and gas reservoirs, whereby oil/gas from low permeability source rocks enters high permeability reservoir rocks, where it may migrate into a trap overlain by an impermeable caprock. Reservoirs so formed may consist of gas only, a gas layer above an oil layer (saturated), or gas mixed in with oil (unsaturated).
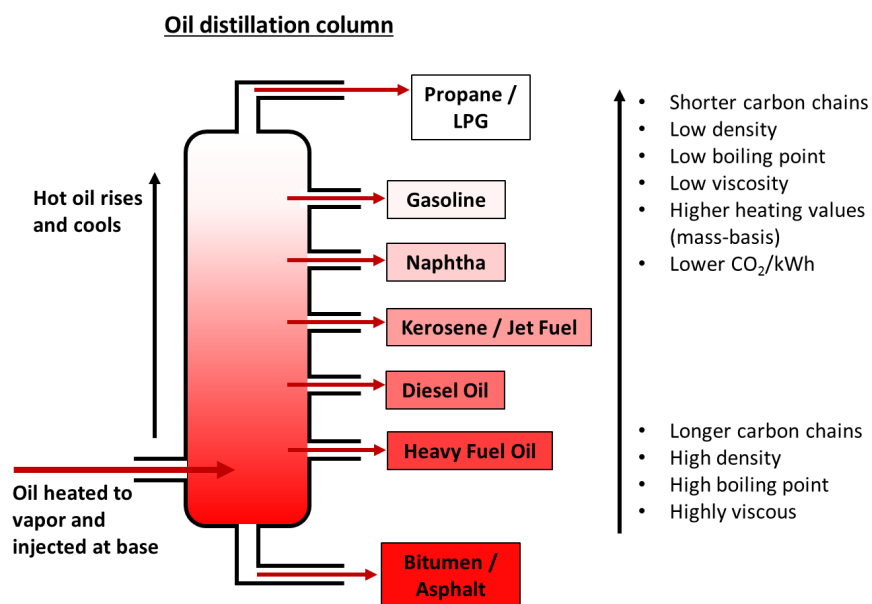

Figure 3.8: Distillation of crude oil into various fractions by density/boiling point.

mainly water and *proppants* (e.g. sand) is injected under high pressure, creating fractures in the shale and/or opening existing fractures. When the injection pressure is relieved, proppants hold the fractures open (see Figure 4.10 in Section 4.6.3).

US oil and gas production have increased dramatically in just the last few years, fueling, especially, increased use of natural gas for electricity generation at the (partial) expense of coal, but whether this is boon or bane is uncertain, for multiple reasons.

Natural gas leakage from fracking, and the larger natural gas system in general, is a point of controversy and uncertainty, and is a major factor undermining the notion of the shale gas revolution being a "green" energy revolution: methane combustion yields only about 55% the CO_2 as coal per kWh of energy produced, and combined cycle natural gas plants are also much more efficient than coal steam plants, yet methane is such a potent greenhouse gas that likely leak rates significantly offset these climate benefits (and at the extreme end of plausibility, overwhelm them entirely). Methane leak from gas exploration is discussed in much further detail in Section 4.6.

The other, and likely even more fundamental, challenge to the green nature of unconventional gas comes from basic economics. Cheap and abundant gas supplies can increase absolute fuel use in all sectors, which can in turn increase total emissions even if the CO_2 emissions per unit of energy decrease. Further, while low cost confers a competitive advantage over coal, gas also directly competes with wind and solar renewables, and building out gas-based infrastructure can "lock-in" gas use for decades to come; this issue is explored in Section 4.6.2. In addition to climatic effects, locoregional water quality may be affected by oil and gas exploration (both conventional and unconventional), and the effect of fracking on water supplies has been extremely controversial (see Section 4.6.3). Thus, there are a variety of negative externalities from both conventional and unconventional fossil fuel extraction. Compared to coal, unconventional gas is almost certainly better for both the climate and for regional water, wildlife, etc.: it is hard to imagine how gas wells could be worse than literal mountain-top removal for coal mining.

3.7.3   Hubbert and Peak Oil

- Fossil fuel reserve discovery and production tends to follows a bell-shaped curve, leading to the concept of "peak oil," as originally formulated by Hubbert.

- Multiple major peaks have already occurred: US conventional crude oil and natural gas production peaked in the early 1970s, and global oil discoveries peaked in the 1960s.

- Nonconventional oil and gas reserves are larger than conventional reserves and have yet to peak, but fossil fuel reserves are so vast that social or political factors must impose extraction peaks for dangerous climate change to be avoided.

While over the vastness of geologic time fossil fuels are to some extent renewable, on the scale of human civilization fossil fuel reserves are finite, and sufficient only for a few more centuries at best, regardless of the environmental consequences of burning them. M. King Hubbert, a geophysicist and geologist for Shell Oil and later the USGS, first warned in 1949 that the finite nature of fossil fuel reserves would shortly necessitate a transition to an alternative energy economy [12], and is most famous for his formulations on oil depletion and peak oil production. In 1956 [56], he correctly projected US conventional crude oil and natural gas production to peak by about 1970, and the idea of "Peak Oil" has since become quite popular in certain quarters, with some anticipating social and political chaos as production of fossil energy begins to fall, reminiscent of the "oil shocks" of the 1970s. While some seem to view Peak Oil as

some inchoate apocalyptic vision of the future, Hubbert's original ideas were straightforward applications of mathematical reasoning to finite resource extraction.

The mathematical basis for Hubbert's work is actually quite simple. He observed that, for a finite resource of size Q, the rate of extraction (or production), P (equal to the rate of change in Q, i.e. $P = dQ/dt$), may initially increase, but at the point that the resource is entirely depleted, $Q = 0$, and P must then also fall to zero. Since P goes to zero, it must at some point hit a maximum and then decline, with this maximum necessarily occurring *before* resource depletion. Hence, "peak oil," in reference to the peak in production rate, or, alternatively, the discovery rate, which had *already* peaked for large US oil fields by the time Hubbert published his work [57]. Indeed, global oil discoveries peaked in the early 1960s, and have almost continuously declined since, with the overall discovery curve roughly bell-shaped [58]. A symmetric curve implies that roughly half of all reserves are depleted at the point of peak production.

Hubbart used a symmetric bell-shaped logistic curve to describe both the rates of oil discovery (i.e. discovery of fields) and production, as introduced in a second 1959 paper [57], which described well the discovery of large oil fields (his earlier 1956 work simply posited a general bell-shaped extraction curve, but did not give any particular mathematical form to it). Under this formulation, to estimate the time to peak oil, one only needs an estimate of total oil reserves and data for cumulative oil production from time zero.

We may conceptually consider our resource, Q, as discovered oil, Q_D, produced or extracted oil, Q_P, and known reserves, Q_R, all having units billion barrels (bbl). The *rates* of discovery and production are given as dQ_D/dt and dQ_P/dt, respectively; under Hubbert's model, discovered or produced oil can be described by a Logistic function,

$$Q_i(t) = \frac{Q_{max}}{1 + ae^{-k(t-t_0)}}. \tag{3.16}$$

Proved reserves are the difference between discovered and produced oil, $Q_R = Q_D - Q_P$. The general forms of the Hubbert curves are shown in Figure 3.9. There is always a lag between discovery and production, and the area under the production curve can never exceed the area under the discovery curve.

While there is debate over when global oil production will peak, it is clear that it must, and Chapman provides a good review of the recent controversies [59]. With respect to global warming, it is also clear that existing fossil reserves are sufficiently vast to cause extremely dangerous climate change well before they are exhausted [60]. Therefore, it seems we are faced with a choice: human civilization must hit fossil energy limits, and very soon (no more than a century or two), but we can hit this limit hard or soft. That is, we can push the climate system into a dangerous and unprecedented (on the scale of agricultural civilization) operating regime by maximally exploiting fuels only to face their exhaustion anyway, or we can preemptively make the transition to a non-fossil energy system. That is, it is essential that the timing of peak oil (and coal and gas) be determined socially and politically, and not by fundamental physical constraints.
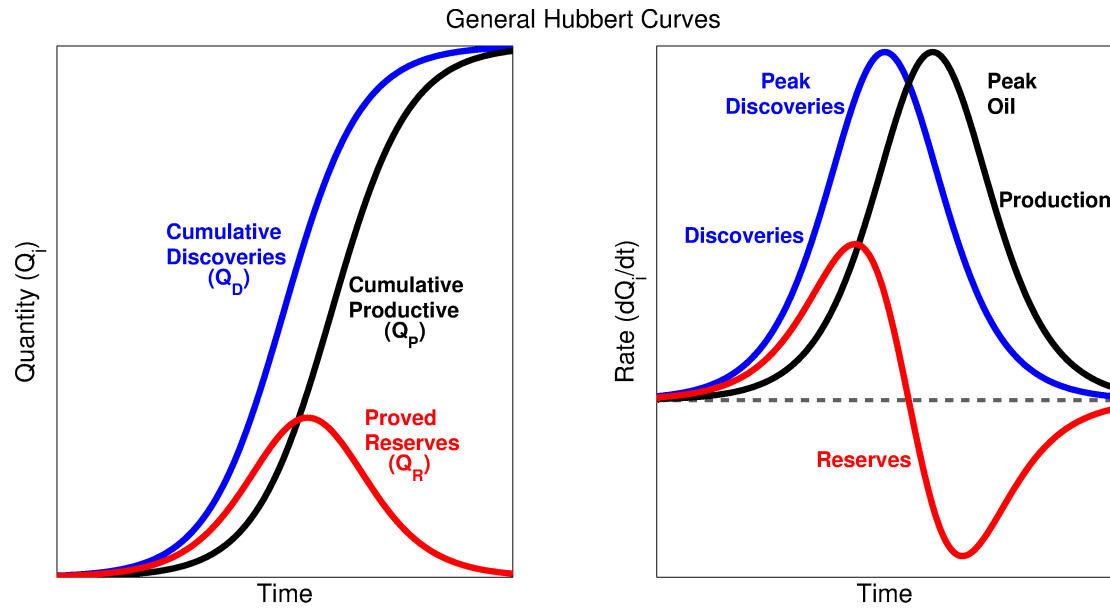
Figure 3.9: General form of Hubbert's curves describing cumulative oil discovery and production (left panel), and the *rates* of discovery/production (right panel). Peak Oil occurs (under the symmetric logistic law) when half of all oil has been produced.
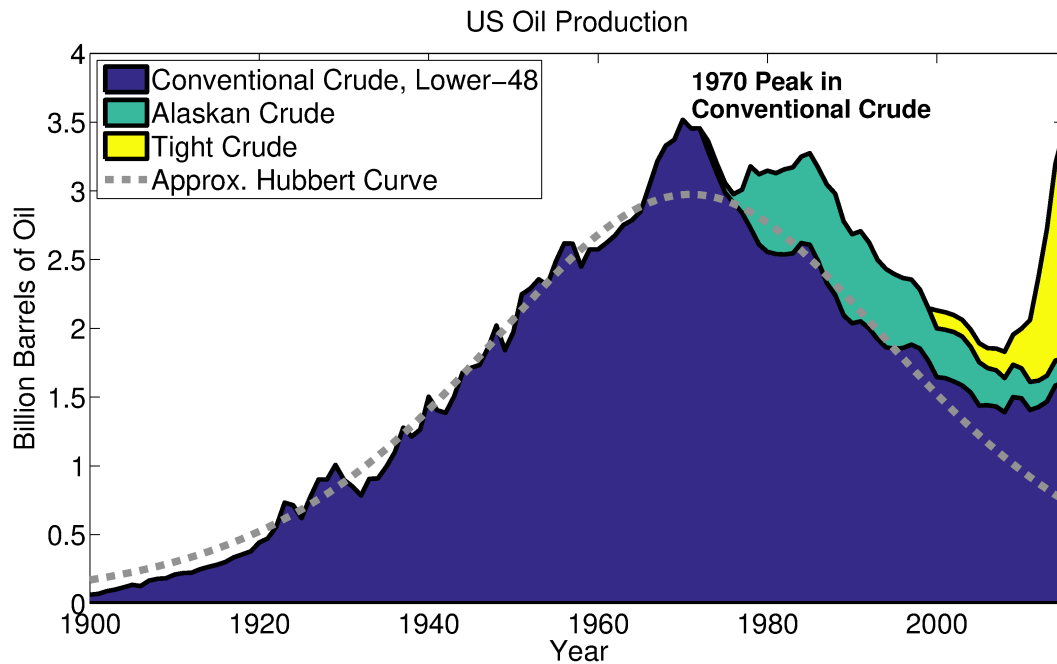
Figure 3.10: US crude oil production from 1900 to 2015. Conventional oil production peaked in 1970, as predicted by Hubbert, and has since fallen, with the recent uptick in production due to exploitation of unconventional tight oil plays. An approximation of Hubbert's curve is superimposed. Alaskan oil is treated separately, as the vast oil fields of the Alaskan North Slope were not discovered until 1968. Alaskan crude production peaked in 1988, and has since dwindled to only about 20% of the peak. Source: EIA.

Figure 3.11: US natural gas production and consumption trends under several disaggregations. The left gives total consumptio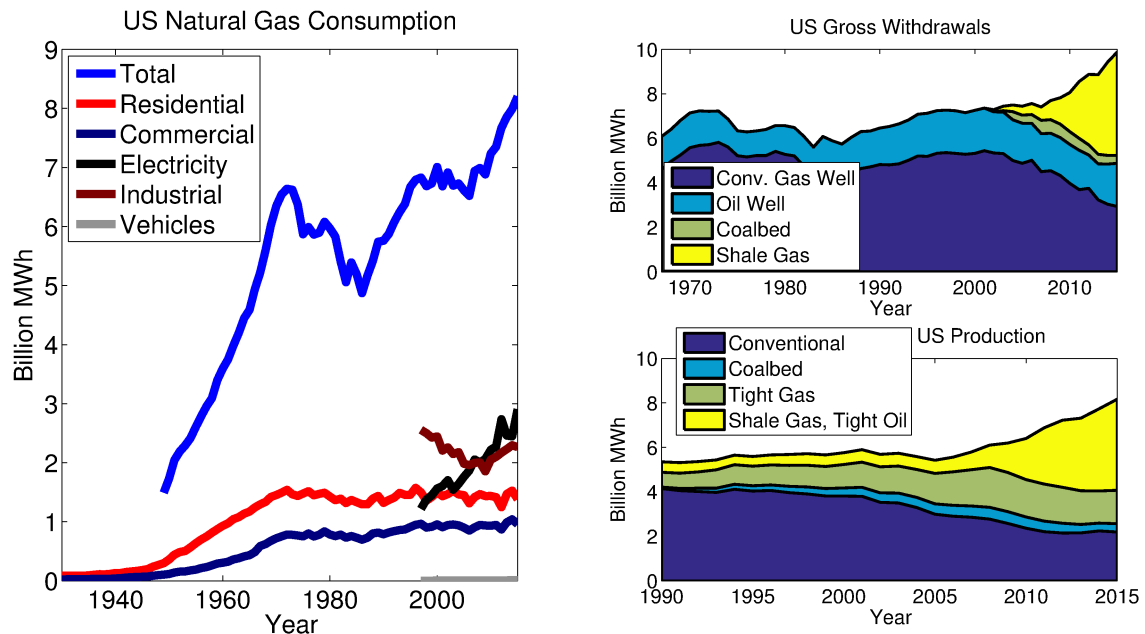n, and consumption by end-use. Note that, in concordance with Hubbert's predictions, conventional gas production peaked in the early 1970s. Source: EIA.

3.8 An introduction to biomass and biofuels

- Of the commonly used biofuels in the US, corn ethanol, soy biodiesel, and wood for heat/electricity, due to the vast land requirements for production, none is capable of significantly displacing US fossil energy use.

- All biofuels, especially corn ethanol and wood for electricity, deleteriously alter ecosystem carbon pools such that it takes decades to centuries before these carbon debts are paid off, if ever. Energy- and emissions-intensive agricultural inputs, such as nitrogen fertilizer, also undermine biofuels' claim to low-carbon status.

- In terms of carbon equivalent emissions, biofuels are probably closer to fossil fuels than to truly low-carbon energy sources, such as wind, solar, some hydro, and nuclear.

Biomass for energy generally consists of woody mass used for heat (either space heating or cooking) and electricity generation (currently a minor but growing energy source, and a major component of short-term renewable energy targets in Europe [47]), and modern transportation biofuels, namely ethanol (almost all of which is derived from corn in the US) and biodiesel (principally from soilbean oil). Currently, about 10% of global primary energy demand is met from biomass in general [62] (wood is the most important component at 6% of primary energy [61]), with the greater part of this use in highly inefficient cook-stoves and open fires throughout the developing world [63]. Such biomass is often harvested unsustainably and degrades forests, impairs indoor air quality, and is a major source of carbon dioxide, carbon monoxide, black carbon, and harmful particulate emissions [63]. In the US, wood is used as a heating fuel for several million households, and waste wood, agricultural byproducts, and forest products are used in wood-fired power plants, or they are co-fired in coal generators. About half the US corn crop is now devoted to ethanol for transportation.

While often promoted as a green and/or zero-carbon alternative to fossil fuels, biomass energy sources often fail to meet either criterion, due to high land and energy requirements for production, and the altered carbon dynamics that result from harvesting and burning. In this section, I review the basic energy conversion efficiencies of different bioenergy sources, and examine their scalability as fossil energy replacements. I also cover some of the alterations in carbon fluxes that result from large-scale biomass for energy projects. Corn ethanol is discussed in further detail in Section 22.3, wood as a residential heat source is treated separately in Section 12.5.6, and woody mass for electricity generation also gets a designated discussion, in Section 4.10.

3.8.1 Scalability of bioenergy sources

It is fairly simple to calculate the potential yields of current energy crops, and hence their feasibility as large-scale replacements for fossil energy. So let us make some of those calculations now.

Soybean biodiesel/fuel oil. Soybean yields in the US on are the order of 3 Mg/Ha, and with 20% of the dry mass lipids [334], we have (assuming 14% moisture content and 37.6 MJ kg^{-1} for lipid [65]) no more than about 6,000 kWh/Ha of oil energy, equivalent to just under 150 gallons of diesel fuel (HHV basis). Per the EIA, the US consumed 60.8 billion gallons of fuel oil/diesel in 2015, as well as 23.7 billion gallons of kerosene-based jet fuel (kerosene and diesel have nearly identical energy content); replacing this with soy oil (and generously assuming that no energy is lost from processing to biodiesel) would require about 575 million Ha, about 75% of the continental US landmass, and 3.5 times the area of *all* US cropland. Using all US land currently devoted to soy production (about 33 million Ha) for biodiesel would displace only 8% of US fuel oil use. Finally, if we wished to replace all US primary energy consumption (29.3 trillion kWa) with soy oil, we would need over six times the US continental land area.

Clearly, soy biodiesel can displace only a few percentage points of current fuel oil use, at best. Adding to the problem, the energy-return on energy-invested (EROI) for US soy biodiesel is probably no better than 5.5 [66], decreasing the effective energy yield of soy biodiesel by 20–25%, and increasing land requirements commensurately.

Soy cultivation for biofuels and animal feed is the major driver of deforestation of the rain forests in Brazil. In addition to being an ecological disaster, clearing of tropical rainforests releases vast quantities of carbon into the atmosphere, incurring a carbon-debt that takes, for soy biodiesel production, *several centuries* to repay even in the best case [70].

Corn ethanol. Corn ethanol suffers from an extremely low EROI, as discussed in Section 22.3, and likely yields no more energy than it takes to produce. This alone should condemn the technology, but for the sake of argument, let us assume that 100% of the energy is recovered. Using calculations detailed in Section 22.3, we see that a 10 Mg/Ha maize yield (typical for the US) gives us just under 21,000 kWh/Ha (HHV basis), or 576 gallons of gasoline equivalent (HHV basis). Therefore, the entire US corn crop could displace about 15% of gasoline used by the light-duty fleet (assumed to be 123.8 billion gallons), while replacing all gasoline would require almost 30% of continental land area and nearly 1.5 times the current US cropland area (for all crops). Again, these calculations are ridiculously biased in favor of ethanol because of its abysmally low EROI. If we assumed a *best-case* EROI of 1.3 [72], then it would effectively take 120% of the US continental land area to replace all gasoline.

Woody biomass. While soy-based fuel oil and ethanol are posited as replacements for liquid petroleum fuels, it would fall mainly upon woody biomass to replace natural gas and coal for heating and electricity generation. Let us assume that wood-fired electricity generation has a 25% thermal efficiency and that non-electrical heating is 70% efficient, and use data from the EIA on natural gas and coal consumption. Further supposing that forest woody net primary

productivity is on the order of 100–300 gC m^{-2} [67], with 200 gC m^{-2} the maximum harvestable (about one-third of mass is lost in the harvest [47]), and using a 11.12 kWh/kgC gross calorific value for wood, to displace all US coal and natural gas use, we would require, in all, 842 million Ha of forest land, while there exist only 302 million Ha of forest in all the US (including the vast forests of Alaska) [639].

Furthermore, appropriating all woody productivity from forests is clearly unsustainable and would decimate forest carbon stocks: an extraction rate of 200 gC m^{-2} corresponds roughly to frequent clear-cutting, and similarly intense logging severely degraded forests in the Pacific Northwest from the 1960s through 1980s [625]. Thus, while burning woody forest products for heat and electrical power is more scalable than modern biofuels, it is still unlikely that they could ever provide more than about 5–15% of such energy at current use rates.

It follows that, in some sense, it is almost irrelevant whether current biofuels are carbon-neutral or not (they are not), as they cannot hope to displace more than a tiny fraction of US (and global) energy use (with the very partial exception of woody biomass). On the other hand, even if they were truly carbon neutral, decreasing carbon emissions by a few percent could *never* (in my view) justify the truly vast tracts of land needed to provide this minuscule benefit. Even "next-generation" biofuels, such as algae, are hopelessly inefficient for meeting current US energy use (see calculations in [65]).

Note that even skeptical analyses, such as that of Schulze et al. [47], who argue that forest biomass cannot sustainably replace even 20% of the world's primary energy demand, typically fail to account for the generally lower thermal efficiency of wood power plants compared to either natural gas or coal. That is, the displacement energy between wood and fossil fuels is not one-to-one, as for example, to generate electricity it takes about 70% more primary wood energy than gas energy for the same electricity yield, under typical power plant efficiencies.

Figure 3.12 graphically illustrates the land bases that would be required to replace several different fossil energy sources with different biofuels (factoring in the EROI for soy biodiesel and corn ethanol), namely replacing diesel, kerosene jet fuel, and fuel oil with soy biodiesel, replacing light-duty vehicle gasoline with ethanol, and displacing natural gas and coal with wood. For comparison, the land bases required to replace all US primary energy or electricity with either solar photovoltaics or wind energy are given[2]. As can be seen, while it would take, in sum, the entire land area of the continental US almost four times over to replace the major fossil fuels with biofuel analogs, solar and/or wind could do the job with just a small fraction of US continental land area (and less than all urban land area, in the case of solar). Note also that wind harvesting directly uses only a small fraction of the land which is harvested, and turbines are commonly placed in agricultural fields.

3.8.2 Carbon dynamics

The burning of biomass to generate power (either motile or electric) has been widely considered a zero emission process, as it is assumed that all carbon liberated from burning plant matter will eventually be reincorporated into plant matter with regrowth. The zero-emissions assumption is erroneous for multiple reasons. In the case of annual crops with short-term carbon cycles, it may reasonably be assumed that all carbon liberated year to year is re-incorporated year to year. However, a seminal paper by Fargione et al. [70] pointed out that, while biofuels such as ethanol or soy biodiesel may be low carbon in this sense, a massive release of carbon occurs when natural ecosystems such as rainforest or grasslands are converted to producing food crops. This conversion creates a carbon debt that was estimated to take anywhere from 17 to 423 years to

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[2]Assuming an average US solar irradiance of 1,800 kWh/m^2 and solar PV efficiency of 15% with a performance factor of 75%, and assuming that 1 W m^{-2} can be harvested by wind turbines.

Soy biodiesel land to displace *fuel oil, diesel, and jet fuel*

- Land Requirement
- US Total Cropped Area
- Soy Crop Area

Factoring in an EROI of 5.5

Corn ethanol land to displace light-duty vehicle *gasoline*

- Land Req.
- US Cropped Area
- Corn Crop Area

Factoring in an EROI of 1.3

Forest land for *wood* to displace natural gas and coal

- Land Req.
- US Forest Area

Solar PV area to displace *all* US primary energy consumption

- Land for All Primary Energy
- Land for All Electricity
- US Urban Area

Wind harvesting area to displace *all* US primary energy consumption

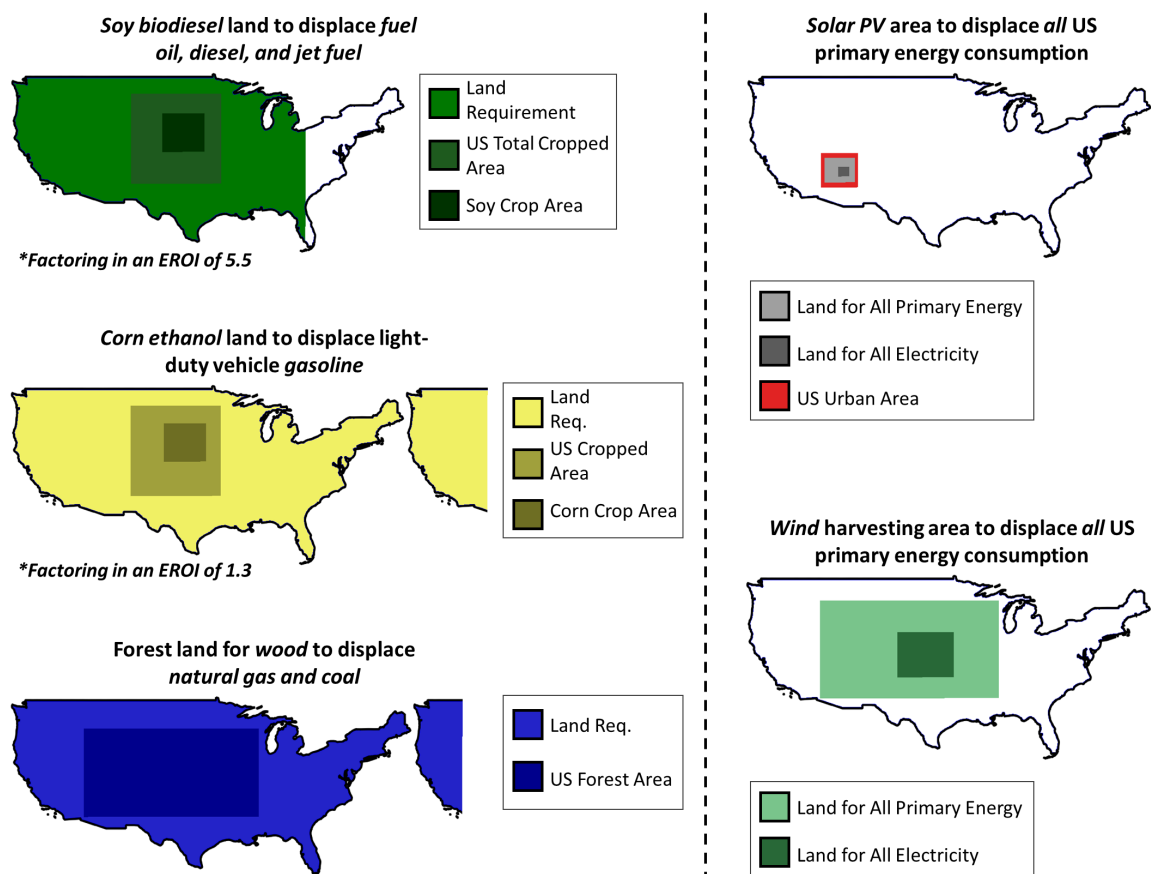- Land for All Primary Energy
- Land for All Electricity

Figure 3.12: Land requirements for current biofuels/biomass options being pursued as replacements for different current fossil energy resources (left panels), and comparisons to land requirements to replace *all* US energy (or just all electricity) using solar or wind (right panels). For soy diesel and corn ethanol, the current cropped areas of soy and corn, as well as the total US cropped area, are also given for comparison. For wood, total US forest area is also provided for comparison, while solar is measured against current US urban area.

repay by offsetting carbon emissions from fossil fuel use, depending upon the habitat converted and the fuel produced. Even if no new land is directly cleared for production biofuels from food crops, this places pressure on the food system that can induce indirect habitat conversion.

Failing to return agricultural residues can also decrease soil carbon stores. Additionally, and as discussed further in Section 22.3.3, in the case of corn ethanol simply abandoning fields likely results in more carbon storage (via soil carbon build-up, and potentially increased above-ground biomass) than could be offset even under optimistic assessments for ethanol, and would have myriad ecology co-benefits.

Vegetation harvested from managed forests, on the other hand, does not necessarily have the problem of associated habitat conversion, but note that converting natural forests to tree plantations *does* decrease soil carbon, biodiversity, and total carbon stores, with one review finding forest plantations to have 28% less total ecosystem carbon [69]. Since this translates into a 291.5 $MgCO_2e$/Ha loss, converting natural forest to a plantation may release even more carbon than clearing grassland for crops [69, 70]. This issue aside, the assumption of zero emissions due to regrowth is highly problematic in the case of forest harvesting: while it may plausibly apply at a *very long-term* steady state, it is clear that, due to relatively slow tree growth, burning forest biomass creates an immediate carbon debt that may take decades or even centuries to repay via regrowth. Furthermore, when forests are continually harvested, there is permanent decrease in the carbon stock of the forest, and thus a permanent carbon shift to the atmosphere. Additionally, harvesting trees from forest also likely deleteriously alters multiple carbon pools other than living vegetation, including deadwood and soil carbon. Under harvesting, mineral nutrients are also continuously lost from the forest system, which will eventually degrade the productivity of the forest [47].

Finally, and perhaps most importantly, the world's forests have proved to be an efficient and continuous carbon sink, especially in Europe and North America, where they are recovering from centuries of deforestation that preceded the transition to a fossil energy system. Harvesting for bioenergy will at least partly undermine this sink. When fully accounting for the fact that old-growth forests likely continue to sequester carbon, and for the effects of harvesting on other forest carbon pools, biomass for electricity may in fact be *worse* for the climate than coal-fired electricity over a time-frame of several hundred years, but this is highly dependent on the forest growth rate and the characteristics of the wood harvest. This issue is explored further in Section 4.10.

3.8.3   Other inputs and emissions

Maintaining high productivity in cropping systems requires significant inputs in the form of fossil energy, fertilizer, and sometimes irrigation. In particular, embodied emissions in nitrogen fertilizer manufacture, and N_2O emissions from its application, can largely offset any carbon benefits from biofuel production. Fossil energy used for farming operations is also significant, while energy for ethanol processing largely cancels out any benefit to this particular fuel. These upstream factors are discussed extensively in Section 22.3.2.

3.9   US primary energy consumption

Having introduced the basics of fossil and biofuels, it seems apropos to close by showing just how dominant fossil fuels have been over the course of the last century and a half, and how dramatically they have increased the total energy available to civilization. Primary energy sources from 1775 through 2011, for the US, are shown in Figures 3.13 and 3.14, based on EIA data [73].
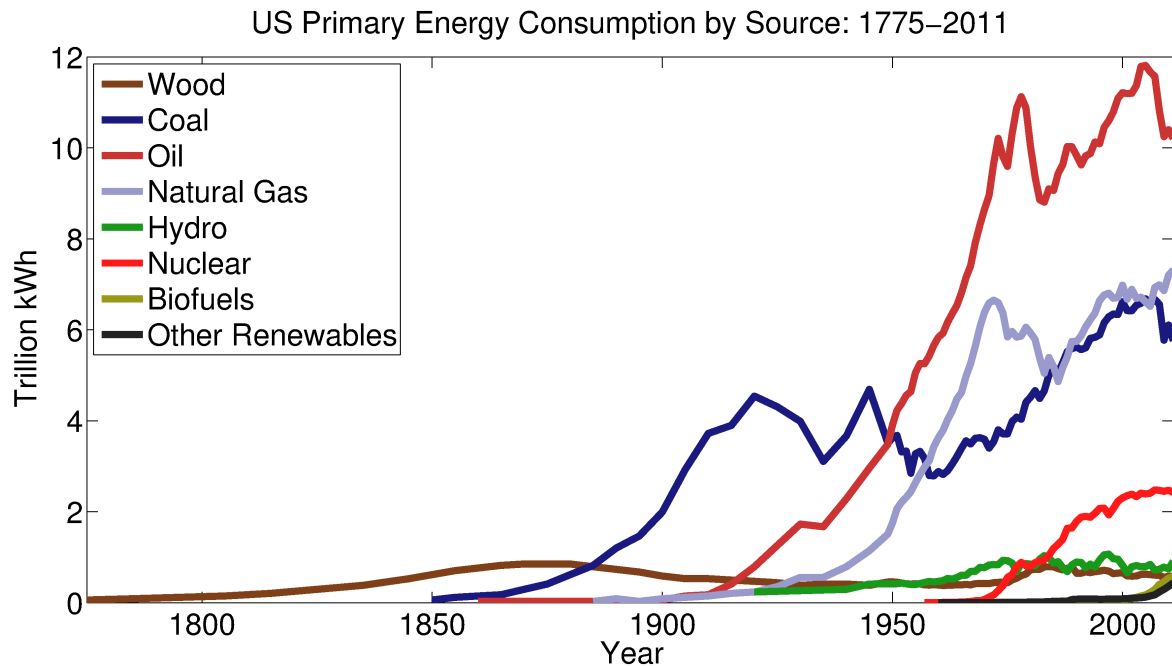
Figure 3.13: Historical primary energy consumption in the US, from 1775 to 2011, based on [73]. Wood was displaced by coal as the top energy source by 1885, while petroleum would overtake coal in 1950. Note the transient peaks in both oil and natural gas in the early 1970s, corresponding to peaking domestic production as well as the "oil shocks" of that era.
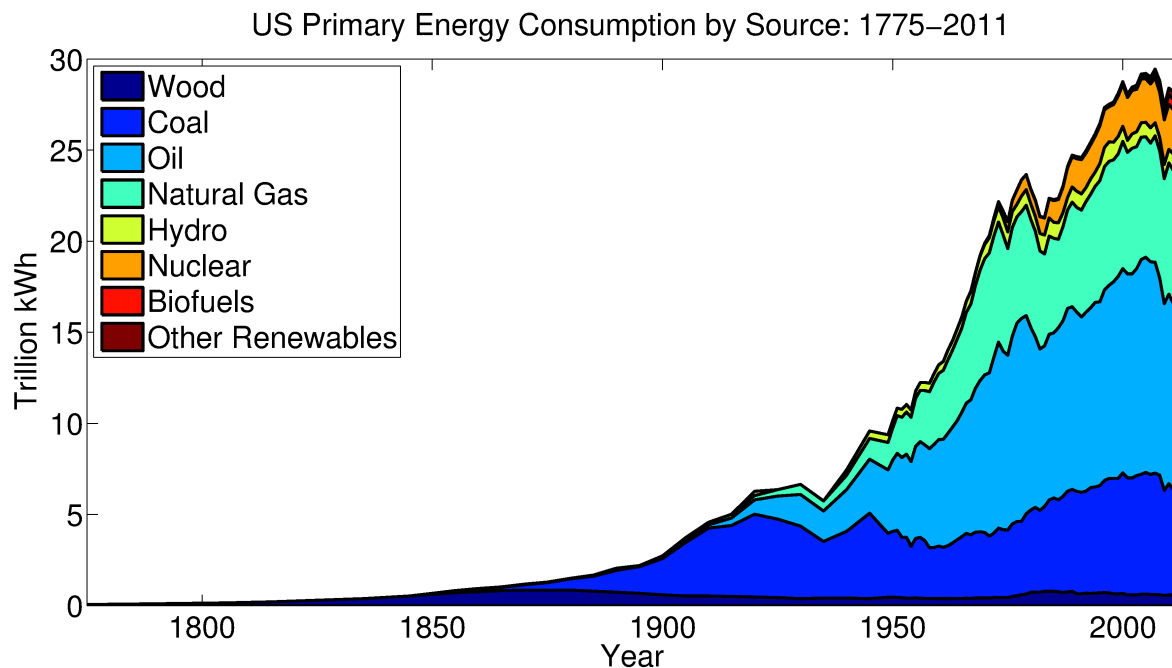

Figure 3.14: Historical primary energy consumption in the US, from 1775 to 2011, mirroring Figure 3.13 but now highlighting the dramatic increase in total energy consumption over the course of the twentieth century.