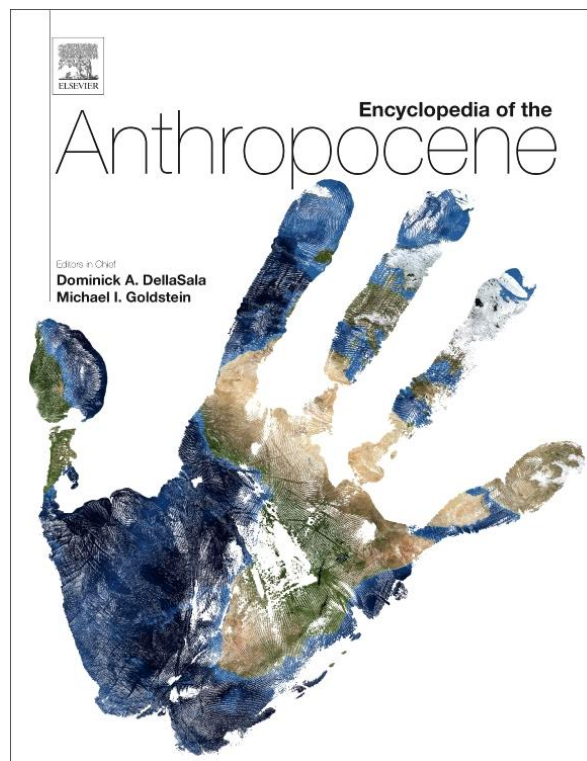


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Combustion to Concentration to Warming: What Do Climate Targets Mean for Emissions? Climate Change and the Global Carbon Cycle

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Introduction

Since 2001, the Intergovernmental Panel on Climate Change (IPCC, 2014) has used a framework that they call “reasons for concern” (RFCs) about rising global temperatures (AR3, AR4, and AR5). The framework is summarized in a diagram whose coloration suggests its nickname: the “burning embers” diagram. The diagram depicts risk levels for five RFCs as a function of the amount of warming in the global mean temperature above conditions in the late 18th century.

The five reasons for concern considered by IPCC in the burning embers diagram are as follows:

- RFC1—risks to unique and threatened systems
- RFC2—risks associated with extreme weather events
- RFC3—risks associated with the distribution of impacts
- RFC4—risks associated with global aggregate impacts
- RFC5—risks associated with large-scale singular events

O’Neill et al. (2017) discuss limitations and levels of risks associated with different amounts of warming within the RFC framework and prioritize future improvements. Risks to unique and threatened systems (RFC1) such as coral reefs, glaciers, and coastal ecosystems rise faster with warming and are better understood than some other risks. Risks to human health and infrastructure associated with extreme weather events (RFC2) and the uneven distribution of impacts to food production (RFC3) rise more slowly but are easy to relate to economic and political disruption. Some of the most severe effects of warming are expected to arise from globally aggregated impacts (RFC4) and from large-scale singular events (RFC5). The IPCC assesses that risks of such destabilizing tipping points as rapid and irreversible coastal flooding, thawing permafrost, and widespread famine are high in this century, but these are the most difficult effects to predict with confidence.

Considering the overall portfolio of risks and the likely costs of mitigation and adaptation to the impacts of climate change assessed by the global scientific community and summarized by the IPCC, 194 countries agreed in December 2015 to limit eventual global mean warming to 2°C above 18th century conditions. Most media coverage of the agreement described the 2°C target as ambitious, but it is hard for even well-educated and informed readers to understand what this target means and why it should be hard to achieve.

Working backward from the 2°C target, how much of the main global warming gas CO₂ does that imply? How is the amount of the gas related to emissions from burning fossil fuels? What happens to the CO₂ we emit after it leaves the smokestacks and tailpipes we associate with these emissions, and how long does the CO₂ remain in the air?

In this article, we explore the relationships among CO₂ emissions, CO₂ concentration, and resulting changes to the Earth system. We consider the fate of fossil fuel CO₂ and how that is related to the sensitivity of the Earth’s climate to fossil-fuel emissions. We dive into some of the uncertainties that keep climate and carbon scientists busy. Finally, we look into the future and think about how answering some of those key questions can help societies develop effective climate policies.

How Sensitive Is the Earth’s Climate to Changes in CO₂?

The absorption of radiation by addition of a unit concentration of CO₂ or other greenhouse gases decreases as the background over which the gas is added increases, because less upwelling radiation is available to be absorbed. Swedish chemist Svante Arrhenius in 1896 first explained this law of diminishing returns based on experiments he conducted himself:

The effect of CO₂ on climate is linear for a geometric increase in the concentration of the absorbing gas.

In other words, we would predict that climate would warm a particular number of degrees not per 100 parts per million (ppm) of the gas in the air but rather per doubling of the concentration. The first 100 ppm we add warms more than the second 100 ppm but changing the concentration from 200 to 400 ppm warms as much as the change from 400 to 800 ppm.

This principle is expressed mathematically as

$$\Delta T = S_{2xCO_2} \frac{\log(C/C_0)}{\log(2)} \quad (1)$$

where $S_{2\times\text{CO}_2}$ is called the *climate sensitivity* to CO_2 in degrees Celsius per doubling of CO_2 , C is the concentration of CO_2 in the atmosphere, C_0 is the baseline CO_2 before warming, and ΔT is the expected increase in global average surface temperature in degrees.

Note that the climate sensitivity considered here relates the eventual warming to the amount of extra CO_2 added to the air, after the energy budget of the entire planet has reestablished equilibrium with incoming solar radiation. This quantity is often called the *equilibrium climate sensitivity*, abbreviated ECS. It is different from the *transient climate sensitivity* (TCS), which is defined as the amount of warming at the time that atmospheric CO_2 crosses the doubling level. The TCS is always less than the ECS. It is much more difficult to estimate the TCS than the ECS, but it may take many decades or even centuries for global warming to reach the levels predicted by the ECS.

It is tempting to try to calculate the climate sensitivity from the earlier equation by simply plugging observed changes in temperature and CO_2 over the past 50 years or so and simply solving for $S_{2\times\text{CO}_2}$. It is often implicitly assumed in popular media that projections of future global warming are produced by such a naive extrapolation from recent warming. There have been efforts to derive climate sensitivity from the modern instrumental temperature record, but these estimates are fraught with uncertainty.

Even the pronounced trend in global mean surface temperatures since 1980 is complicated by interannual and decadal variations that are not caused by the enhanced greenhouse effect. Choosing different starting and ending years from this noisy time series leads to substantial differences in the calculated warming. Worse, the change in CO_2 over this period is rather small on a percentage basis. In 1980, the annual average CO_2 concentration measured at the Mauna Loa Observatory high atop a mountain in Hawaii was 340 ppm. In 2017, it has risen to 405 ppm: an increase of just 18% or less than one-fourth of one doubling. Since we are trying to estimate the warming per doubling (100% increase), any error we make in attributing just the CO_2 -related warming over the period since 1980 will be amplified fourfold when we extrapolate from this period to a full doubling.

A much more reliable approach to estimating climate sensitivity is to reframe the question and focus on the amount of warming per unit of radiation imbalance rather than per doubling of CO_2 . This has the conceptual advantage that it allows us to focus on the actual cause of the warming (heat). More importantly, we are no longer limited in our investigation to error amplification due to extrapolating from the relatively small recent changes in CO_2 and temperature.

Climate Forcing, Response, Sensitivity, and Feedback

Climate scientists define *climate forcing* as an imbalance in radiation at the top of the Earth's atmosphere. Climate forcing is the difference between the rate of energy received by absorption of solar radiation and the rate of energy emitted by the top of the Earth's atmosphere, expressed in watts per square meter (W m^{-2}). If the Sun were to brighten slightly so that Earth absorbed 1 W m^{-2} more of its radiation, climate would warm until outgoing emission of infrared radiation balanced this forcing. Conversely, if the Earth's reflectivity (albedo) increased slightly due to changes in clouds or ice cover, climate would cool, reducing thermal emission until radiative equilibrium was reestablished. We define *climate response* as the change in globally averaged surface temperature that results from climate forcing due to radiation imbalance at the top of the atmosphere.

We can now define climate sensitivity to radiation as the ratio of climate response to climate forcing:

$$S = R/F \quad (2)$$

where R is climate response (degrees of global average warming in Celsius) and F is climate forcing (in W m^{-2} of radiation imbalance at the top of the atmosphere).

Two Ways to Estimate Climate Sensitivity

Fundamentally, there are two independent ways to estimate the sensitivity of the Earth's climate to changes in the radiation budget of the planet by

- (1) direct calculation using known laws of physics,
- (2) using observations of past climate change.

Both methods are important; the science behind both approaches is quite mature. Fortunately, the two methods are quite complementary, with the advantages and disadvantages of each method compensating pretty well for one another.

Earth System Models

The first method is called climate modeling. Starting from Newton's equations of motion, thermodynamics, and radiation physics, scientists have devised detailed numerical simulations of the Earth's climate system. The fundamental equations have been well-known since the 19th century, and complete numerical models of the circulation of the global atmosphere have been in use since for about 50 years. In the 1980s, climate models began to include a completely interactive ocean. In the 21st century, these models include fully coupled representations of soil, vegetation, clouds, rain, snow, air pollution, and ice sheets. These more fully functioning models are known as "Earth system models" (ESMs), and there are dozens of them in use at major research centers around the world (Heavens et al., 2013).

The key advantage of using ESMs to calculate climate sensitivity is that scientists can experiment with the many components of the Earth's climate system to better understand and predict the effect of different physical mechanisms. For example, we can perform one experiment in an ESM in which we change the brightness of the Sun while holding cloud properties constant. Then, we can perform a second experiment in which we allow cloud properties to change in response to the added solar heat and thereby gain insight into the role that clouds play in enhancing or suppressing the warming impact.

The disadvantage of using ESMs to estimate climate sensitivity is the tangled web of complex causes and effects that arise from all of the interacting positive and negative feedbacks in the Earth's climate. There are many such interacting processes in the Earth system (Roe, 2009). An initial addition of heat can cause further changes that then add or subtract additional heat. Processes that add to initial warming are called "positive feedback," whereas processes that subtract from the initial warming are called "negative feedback." An example of positive climate feedback is the tendency of warmer air to evaporate more water from oceans and vegetation, which adds to the initial warming (a positive feedback) because water vapor is a powerful greenhouse gas. Another obvious example is that initial warming may melt some snow and ice. Since snow and ice are bright, they reflect a lot of incoming sunlight to space. Melting snow and ice therefore darkens the planet's surface, allowing more sunlight to be absorbed and adding to the initial warming (another positive feedback). By contrast, if some of the extra water vapor evaporated from the oceans as a result of warming condensed to form low clouds and fog, these might reflect more sunlight to space and subtract from the initial warming (a negative feedback). Calculating the overall impact of all of these positive and negative feedbacks in the Earth's climate system is complicated and difficult. Estimates of climate sensitivity obtained from ESMs will always depend on model details that are uncertain.

Thousands of experiments with ESMs have been published over the past 50 years. The overall climate sensitivity derived from these studies is in the range of $0.4\text{--}1.2^\circ\text{C/W m}^{-2}$. Since doubling CO_2 reduces outgoing infrared emission of the Earth by 3.7 W m^{-2} , these studies support a climate sensitivity of about $1.5\text{--}4.5^\circ\text{C}$ per doubling of CO_2 .

Paleoclimate Analogs

A separate branch of science that deals with climate of the past has grown out of geology. Rocks, sediments, and fossils contain abundant information about periods of both warming and cooling in the Earth's past. If we can use these data to estimate both the forcing and response of these past climate changes, we can estimate the sensitivity of the Earth's climate.

The great advantage of using paleoclimate proxies to estimate climate sensitivity is that all the feedbacks are included. Since this method uses the climate history of the real Earth, a model of the complex interacting feedback processes is not needed. Using real climate changes of the past allows the overall sensitivity to be estimated but provides none of the mechanistic detail we get from ESMs.

The major disadvantage is that major changes in Earth's climate happened a long time ago, before reliable records were kept, and it is difficult to get global records of both climate forcing and response for these events. Generally, we have more information about climate changes in the relatively recent past, because sediments and fossils may still be undisturbed from those events than for changes in the very distant past.

An excellent example of past global warming that can be used to estimate climate sensitivity is the period from about 18,000 to 8000 years ago. During the Last Glacial Maximum (LGM) 18,000 years ago, huge ice sheets covered parts of North America and Eurasia, and sea ice covered large areas of the North Atlantic and North Pacific Oceans. Ten thousand years later (8000 years ago), the ice had retreated to its modern boundaries.

We have three key pieces of information from the LGM that allow us to reconstruct climate forcing, response, and sensitivity for the warming at the end of the last Ice Age (Hansen et al., 2013):

- (1) The extent of the land and sea ice that melted
- (2) Changes in greenhouse gases in the atmosphere that accompanied the warming
- (3) Changes in temperature over both land and oceans during those 100 centuries

The ice sheets of the LGM carried sand and gravel that was deposited in mounds and ridges at their margins, forming characteristic sediments. These glacial sediments have been carefully charted across the northern hemisphere, allowing us to map the extent of the ice sheets. Knowing which parts of the world changed from ice sheets and sea ice to land and open ocean allows us to calculate the change in the Earth's albedo (reflected sunlight). From these maps, we can quantify the amount of extra sunlight absorbed as a result of the melting of the snow and ice. This added absorption is a key ingredient of climate forcing, in W m^{-2} .

Changes in atmospheric greenhouse gases during this warming period can be measured because, amazingly, we have actual samples of fossil air from the LGM and the period that followed. Air trapped between ancient snowflakes was gradually sealed off as snow compacted to ice, becoming bubbles in ice sheets that still persist in Antarctica and Greenland. Since the 1980s, scientists have extracted cores from these ice sheets and analyzed the air in those bubbles. We can now reconstruct the changes in greenhouse gases over the whole period of deglaciation and back almost 800,000 years before. As the ice melted, these gases were released from the oceans in which they had been dissolved, reducing the transparency of the atmosphere to infrared radiation. This is the second main component of climate forcing after the LGM, in W m^{-2} .

Fossils of microscopic marine plants and animals constantly rain down onto the ocean bottom, becoming buried in seafloor sediments. On land, pollen blows from trees and other plants and is sometimes preserved in lake beds or other deposits. Scientists

have combed through these microfossils from both land and oceans, cataloging the assemblages of plants and animals in each layer. These studies have allowed us to reconstruct the distribution of temperatures as global maps over different times during and following the last ice age. These maps of paleotemperature are the basis for our estimation of the total climate response (including all the feedbacks) that resulted from the albedo and greenhouse forcing.

Based on the mapping of glacial sediments, we know that melting ice and snow after the LGM added about 3.5 W m^{-2} of absorbed solar radiation to the Earth. From the changes in ice core bubbles, we know that rising CO_2 and other gases added another 3 W m^{-2} of infrared absorption. These combined for a total forcing of 6.5 W m^{-2} between 18,000 and 8000 years ago. From the paleotemperature maps derived from microfossils, we know that the Earth's surface temperature warmed by about 5°C in response to the albedo and greenhouse forcing during deglaciation. The overall climate sensitivity obtained from these data is just the retain of the response to the forcing: $(5^\circ\text{C})/(6.5 \text{ W m}^{-2}) = 0.8^\circ\text{C/W m}^{-2}$. Multiplying this by the expected 3.7 W m^{-2} of climate forcing per doubling of CO_2 gives an estimate of 2.8°C of warming per CO_2 doubling.

There are many other periods of climate change in the Earth's geologic past that provides independent estimates of climate sensitivity, ranging over hundreds of millions of years. Scientists have also devised clever ways to estimate climate sensitivity from variations on shorter periods in recent decades. A systematic review of all of these estimates by Knutti and Hegerl (2008) found a range of $1.5\text{--}4.5^\circ\text{C}$ per doubling of CO_2 and a most likely value around 3°C per CO_2 doubling, which is quite consistent with estimates obtained from ESMs. This confluence of independent estimates of climate sensitivity from physics-based ESMs and geology-based paleoclimate proxies grounds modern climate science.

Relating Warming and CO_2 Concentration in the Atmosphere to Fossil-Fuel Combustion

Given the internationally agreed target for limiting CO_2 -induced warming to no more than 2°C above preindustrial conditions, we can use the estimate of 3°C of warming per doubling of CO_2 derived above to calculate that we need to limit CO_2 to no more than two-thirds of a doubling.

From the ice cores discussed in the previous section, we know the CO_2 concentration was about 280 ppm before the industrial revolution. Rearranging Eq. (1), we can then substitute $S_{2x\text{CO}_2} = 3^\circ\text{C}$ and $C_0 = 280$ ppm, to find a future amount of CO_2 at which we need to stabilize concentration to limit warming to our target:

$$\begin{aligned}\log(\text{CO}_2/C_0) &= \Delta T/S_{2x\text{CO}_2} \times \log(2) \\ \log(\text{CO}_2) - \log(280) &= 2/3 \times \log(2) \\ \log(\text{CO}_2) &= 2/3 \times \log(2) + \log(280) \\ \text{CO}_2 &= 10^{[2/3 \times \log(2) + \log(280)]} = 455 \text{ ppm}\end{aligned}$$

So, to limit eventual global warming to 2°C , CO_2 needs to stop rising at about 455 ppm. Some countries are also pushing for a 1.5°C limit to warming. Using the simple calculation in the preceding text, this would require limiting atmospheric CO_2 to 396 ppm. As of this writing, the global average CO_2 concentration is about 405 ppm, so the lower target seems unrealistic. As we will see in the succeeding text, even constraining global warming to 2°C will be difficult.

To understand how this limit can be translated to emissions from fossil-fuel burning, we have to do some algebra.

In 2015, the global economy consumed about 10 GtC per year in the form of coal, oil, and gas [LeQuere et al., 2016]. One gigaton is 10^9 (metric) tons, or 10^{12} kg, or 10^{15} g. It is sometimes also called a petagram. A common source of confusion is that many economists and policy specialists use the unit GtCO_2 , which includes the mass of the oxygen and the carbon in CO_2 . From the atomic weights of the elements, it is easy to calculate that $1 \text{ GtC} = 3.7 \text{ GtCO}_2$. The current rate of global fossil-fuel combustion is 10 GtC year^{-1} or $37 \text{ GtCO}_2 \text{ year}^{-1}$.

To calculate the amount by which burning 1 Gt of carbon will change the concentration of atmospheric CO_2 , we divide the mass of carbon burned by the mass of the atmosphere:

$$\text{change in } \text{CO}_2 = M_C / M_{\text{air}} = 10^{12} \text{ kg C} / 5.14 \times 10^{18} \text{ kg} = 1.95 \times 10^{-7} \text{ kg C/kg air}.$$

Concentrations of trace gases in air are typically reported in moles per mole instead of kilogram per kilogram. The conversion is accomplished by dividing the mass of each component by its molecular weight:

$$1.95 \times 10^{-7} \text{ (kg C)/(kg air)} = (1.95 \times 10^{-7} \text{ kg C} / 12 \text{ g/mol} / 1000 \text{ g/kg}) / (\text{kg air} / 29 \text{ g/mol} / 1000 \text{ g/kg}) = 0.47 \times 10^{-6} \text{ mol } \text{CO}_2 \text{ per mol air}.$$

Because there is so little CO_2 in the air, it is customary to report this change in CO_2 as 0.47 ppm by moles, which is the same as parts per million by volume.

This leads to a very useful "rule of thumb"—adding one GtC to the air changes its CO_2 concentration by a little less than one-half ppm.

If setting carbon on fire by burning fossil fuels was the only way to change CO_2 in the atmosphere then, we could easily calculate the amount still remaining to burn to achieve the 2°C limit to which the world's governments have committed. As we saw in the preceding text, CO_2 would have to stop increasing at 455 ppm, about 50 ppm higher than it is now. Using our rule of thumb that each GtC burned adds about one-half ppm, only about 100 more GtC of coal, oil, and natural gas can be burned if eventual global warming is to be limited to 2°C .

The global economy currently produces about 10 GtC year^{-1} of CO_2 from fossil-fuel combustion (Le Quere et al., 2016), so limiting ourselves to 100 GtC would mean we have only about 10 years' worth of emissions at the current rate. Luckily, the oceans and land ecosystems provide some buffer by removing about half of the fossil CO_2 emitted by combustion. To understand the processes that provide this valuable service to the world economy, we need to review the overall cycling of carbon in the Earth system in the next section.

The Global Carbon Cycle

Nearly all of the carbon near the surface of the Earth is locked up as calcium carbonate (CaCO_3) in sedimentary rocks (limestone) that do not readily exchange carbon with the atmosphere, with the ocean, or with the plants and soils. These latter three are called the "labile" reservoirs of carbon on Earth, because their carbon can easily pass from one to another through various natural processes (see Fig. 1).

The oceans contain most of the labile carbon: about $38,000 \text{ GtC}$, about 90% as dissolved bicarbonate ion (HCO_3^-) and 10% as carbonate ion (CO_3^{2-}). Plants and soils on land contain about 2000 GtC , of which perhaps one-third is alive (plants, microbes, animals), and two-third is dead organic matter (Ciais et al., 2013). Before the industrial revolution, the atmosphere contained about 600 GtC (about 280 ppmv) in the form of CO_2 gas. In 2016, the concentration of CO_2 was about 405 ppmv , so the atmosphere now contains about 860 GtC as CO_2 .

Photosynthesis is the process by which plants convert inorganic CO_2 into organic molecules like sugar, which is the basis for nearly all life on Earth. Plants consume about 120 GtC of atmospheric CO_2 each year to build their tissues and conduct their life processes. Ecologists call this total gross primary production (GPP). Remarkably, this means that about one-seventh of all CO_2 molecules in the atmosphere are converted to plant material every year, so that without some other process to replenish it, all the CO_2 in the atmosphere would be completely consumed in just 7 years! Of course, this does not happen because the plants respire about half of the CO_2 they fix through photosynthesis, and then, when plants die, the other half is respired by the microbes and other animals that eat them. Over geologic time, a tiny excess in global photosynthesis and global respiration and decomposition leads to storage of fossil carbon in sedimentary rocks. These "fossil fuels" (coal, oil, and gas) have been accumulating in the rocks for hundreds of millions of years, and now, people are busy digging them up and burning them to supply energy to the global economy.

A lot of CO_2 also dissolves into the oceans each year, mostly where the surface water is very cold (in the Arctic and Antarctic). Carbon dioxide is about twice as soluble in freezing cold water than it is in warm tropical water, for the same reason that soda or beer left on a kitchen table goes flat as it warms up. Cold polar water is also dense so that the CO_2 -enriched waters sink to great depth in the world oceans. About $1/1000$ of the mass of the oceans is chilled in this way each year, carrying dissolved CO_2 into the deep ocean. This sinking motion displaces an equal amount of water at depth that is forced to rise in the tropics where the CO_2 comes out of solution as the cold water warms in the tropical sun. About 90 GtC year^{-1} dissolves into cold waters, and about 90 GtC year^{-1} outgasses from warm water.

Samples of fossil air have been recovered from tiny bubbles in ice cores taken from Greenland and Antarctica. These samples reveal that before the industrial revolution, the amount of CO_2 in the atmosphere was very steady for thousands of years, at about 280 ppm . From these ice core measurements, we know that the rates of CO_2 uptake by plant growth was almost perfectly balanced by the rate of decomposition of dead plants, and that the rate of CO_2 dissolving into cold polar oceans was almost perfectly balanced by the rate of CO_2 outgassing from warm tropical oceans.

Global Carbon Cycle

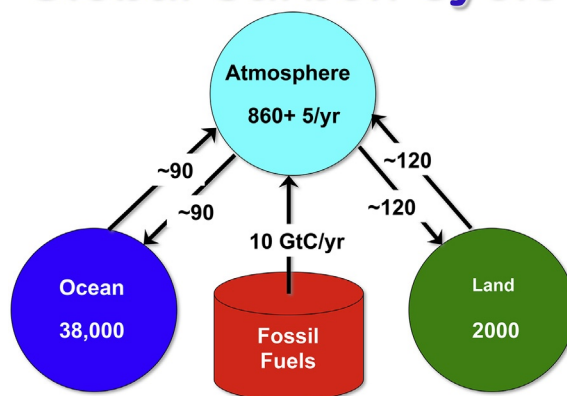


Fig. 1 The contemporary global carbon cycle. Four labile pools are shown: the atmosphere, land biosphere, oceans, and fossil fuel reservoir. Numbers associated with each pool are total carbon storage in Gigatons of carbon (10^{12} kg). Arrows indicate flows among these pools in Gigatons of carbon per year ($10^{12} \text{ kg C year}^{-1}$). Data are averaged over the past several years as reported by the Global Carbon Project (Le Quéré et al., 2015).

CO₂ Removal by Land and Oceans

Instruments capable of making precise determination of the concentration of CO₂ in ambient air were first developed in the 1950s, and routine measurements began at Mauna Loa in Hawaii in 1959. It quickly became clear that atmospheric CO₂ was increasing. By the mid-1960s, scientists had determined that the rate of increase of CO₂ was only about half the global rate of fossil-fuel combustion. What was happening to the other half, the so-called missing carbon?

Early speculation was that the missing carbon (half of fossil-fuel emissions) must be dissolving into the oceans. This makes sense because as atmospheric CO₂ increases, ocean waters become undersaturated relative to the air. Oceanographers were soon able to rule out the idea that the oceans were absorbing half of fossil-fuel emissions.

There are three different atomic forms of carbon. By definition, all carbon atoms contain six protons. The most common form (¹²C) also contains six neutrons, weighing 12 g/mol. About 1% of all carbon atoms (¹³C) contain seven neutrons instead of six. Both ¹²C and ¹³C are stable, meaning that they are not radioactive. A very small percentage contains eight neutrons instead. This ¹⁴C is radiocarbon, which is produced from atmospheric nitrogen by cosmic ray bombardment and then decays with a half-life of about 5500 years.

When plants convert CO₂ to sugars by photosynthesis, they “prefer” ¹²C to the heavier isotopes of carbon. This is partly because the lighter CO₂ diffuses more easily into the tiny pores (stomata) in plant leaves and partly because of slightly different biochemical reaction rates in chloroplasts. As a result, all plant carbon is slightly depleted in ¹³C, and since fossil fuels are derived from plants, they are ¹³C-depleted as well. By the mid-1960s, oceanographers were able to measure the slow but steady changes in ¹³C dissolved in seawater due to the addition of billions of tons of fossil plant carbon to the atmosphere by burning coal, oil, and gas.

In 1963, the United States and the Soviet Union agreed to stop testing nuclear weapons in the atmosphere. Before the treaty went into effect they each conducted a large number of bomb tests, which unleashed a spike in atmospheric ¹⁴CO₂. Oceanographers have traced the penetration of the bomb radiocarbon spike through air–sea gas exchange, marine biology, and deep-sea mixing.

Careful tracking of both ¹³C-depleted fossil carbon and the bomb ¹⁴C spike show that CO₂ exchange with the oceans can only account for about half the “missing carbon” that is emitted by fossil-fuel combustion but does not show up in the atmosphere. Subsequent studies using both direct measurement of carbon species in seawater and numerical modeling of the relevant chemistry and circulation have confirmed this early result. The rest of the missing carbon must be accumulating in land ecosystems (plants and soils) as discussed in the succeeding text.

The annual global budget of carbon in the Earth system is shown in Table 1 and in Fig. 1 based on data reported by Le Quéré et al. (2016). Global emissions from combustion of fossil fuels are about 10 GtC year⁻¹. Half of that total (about 5 GtC year⁻¹) accumulates in the atmosphere, raising the concentration of atmospheric CO₂ by about 2.5 ppm. Half of the fossil-fuel emissions are sequestered in land ecosystems and oceans, with roughly one-fourth of CO₂ emissions accumulating in each. These net losses of fossil-fuel CO₂ from the atmosphere (about 2.5 GtC year⁻¹ into both oceans and land) are much smaller than the gross two-way fluxes associated with photosynthesis (about 120 GtC year⁻¹) or air–sea gas exchange (about 90 GtC year⁻¹).

Ocean Carbon Sequestration

When CO₂ dissolves in seawater (see Box 1), it forms carbonic acid (H₂CO₃), most of which then dissociates to form a hydrogen ion (H⁺) and a bicarbonate ion (HCO₃⁻). A small fraction of the bicarbonate undergoes a second dissociation to form another hydrogen ion and a carbonate ion (CO₃²⁻). This “weak acid buffering” of carbonic acid has long been studied in the laboratory and is intimately linked to ocean pH and alkalinity. Nearly all the CO₂ that dissolves into the ocean (primarily in cold regions) is balanced by degassing (primarily from warmer regions). Part of the net uptake of 2.5 GtC year⁻¹ by the oceans results from the slow sinking of very cold polar waters, which oceanographers call the “solubility pump.” The rest is due to the “biological pump” (Volk and Hoffert, 1985). Phytoplankton and other plants convert dissolved CO₂ into organic matter, which passes through food webs as it is eaten by zooplankton and other organisms. About 90% of this organic carbon is converted back to dissolved CO₂ in the well-lit “photic zone” of the uppermost ocean, where it is then available to reequilibrate with the atmosphere or to be taken up by other plants through photosynthesis. A small fraction of the carbon fixed by marine biota sinks below the photic zone and sequestered into the dark depths that have no physical contact with the atmosphere over many centuries.

Land Carbon Sequestration

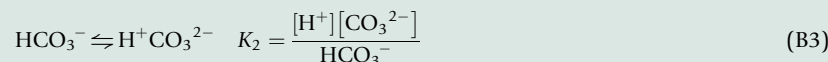
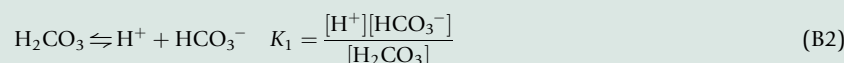
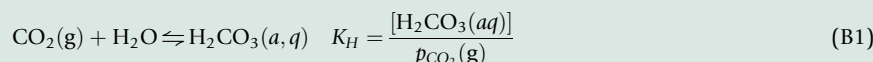
The planetary-scale sequestration of fossil carbon in land ecosystems was a major surprise that is hard to explain but required by mass balance of carbon in the atmosphere and oceans. Photosynthesis converts huge amounts of carbon into plants every year, but

Table 1 Annual budget of carbon exchanges in the Earth system

Fossil-fuel emissions	10 GtC year ⁻¹
Accumulation in atmosphere	5 GtC year ⁻¹
Net uptake in oceans	2.5 GtC year ⁻¹
Net uptake by land ecosystems	2.5 GtC year ⁻¹

Box 1: Carbonate Chemistry in the Oceans

When CO₂ dissolves in seawater, three reversible chemical equilibria determine the resulting concentrations of several important chemical species (Tans 1998):

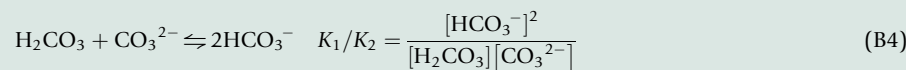


Dissolved carbon dioxide produces the weak acid H₂CO₃ (reaction B1). Carbonic acid dissociates to form bicarbonate ions (HCO₃⁻) and H⁺ ions (reaction B2). The bicarbonate further dissociates to form carbonate ions (CO₃²⁻) and additional hydrogen ions (reaction B3). Free hydrogen ions released by these reactions depress the ocean pH.

The pH of the oceans is currently about 8.1. Under these conditions about 90% of the dissolved inorganic carbon (DIC) in the oceans is in the bicarbonate form, and about 10% is carbonate ion. Very little of the DIC in the oceans is undissociated carbonic acid.

The equilibria among these three forms of DIC in seawater are responsible for the vast storage of carbon in the oceans (about 38,000 GtC) compared to the atmosphere (about 860 GtC).

This is easy to understand by combining second and third equilibrium relationships in the preceding text to give



This final reaction indicates that when CO₂ is added to seawater to form carbonic acid, carbonate ion is consumed to form two bicarbonate ions. As more CO₂ is added to the atmosphere and progressively dissolves into the ocean, it is immediately transformed to bicarbonate. Without this reaction, CO₂ would equilibrate between the oceans and atmosphere and the Earth would be very different!

Reaction (B4) shows that as long as there is sufficient carbonate in seawater, the oceans can dissolve more CO₂ from the atmosphere by converting it to bicarbonate. Conversely, dissolving CO₂ consumes carbonate ions. Taking this process too far would produce several unfortunate biogeochemical consequences. First, depression of seawater pH and depletion of dissolved carbonate ion enhance the solubility of calcium carbonate (CaCO₃). Many marine plants and animals make their shells and skeletons from this mineral, and long before they actually dissolved, they would starve due to the increased energy requirements of extracting CaCO₃ from the caustic water. Secondly, depletion of carbonate ion in the water reduces the solubility of CO₂. This reaction limits the ultimate capacity of seawater to absorb fossil-fuel CO₂, at least until more CaCO₃ from sediments can dissolve over geologic time to replenish the system.

the persistent terrestrial sink that has been documented over the past half century means that at the scale of the whole Earth, plants have been growing faster than they are dying. Until the mid-1980s, most ecologists were convinced that the converse was true: it was widely believed that deforestation and development were destroying biomass faster than it could be replenished.

Four leading mechanisms for long-term carbon sequestration on land have been documented (Ciais et al., 2013) in the three decades since it became clear that the rate of plant growth exceeds that of death and decomposition:

- (1) CO₂ fertilization
- (2) Nutrient fertilization
- (3) Land use change
- (4) Boreal warming and greening

The simplest and oldest idea to explain net carbon sequestration on land is CO₂ fertilization: since plants eat CO₂ for a living, they simply eat more when CO₂ is more abundant. Measurements in the laboratory show that this is certainly the case at the molecular and cellular levels: the biochemical reactions of photosynthesis run faster at higher CO₂ concentration. Greenhouse experiments show that well-watered and well-fed plants that are protected from pests and competition and weather do indeed grow faster in elevated CO₂. What is more surprising is that whole outdoor plants, landscapes, and indeed, the entire planetary biosphere should behave this way. The growth of most wild plants and landscapes is limited by other resources besides CO₂: nutrients, water, light, soil, and frost-free weather.

CO₂ fertilization experiments have now been conducted over dozens of outdoor ecosystems around the world using a technique called free air carbon enrichment (FACE). A ring of towers is constructed to fumigate the air with CO₂, with sensors and control technology that hold concentrations constant in the ring 24 h a day for several years. Carbon storage in leaves, stems, roots, and soil organic matter is compared over time with rings enclosing similar plant communities under different CO₂ levels. Most of these studies have shown an initial increase in growth rates under elevated CO₂, slowing to match control conditions after a few years as other resources (especially nitrogen) become limiting.

As it turns out, humanity has been aggressively fertilizing the global biosphere with nitrogen as well as carbon for many decades. Part of this is intentional: since the invention of the Haber-Bosch process for "fixing" nitrogen from chemically inert N₂ in the early 20th century, artificial nitrogen fertilizer has become the biggest source of bioactive nitrogen on Earth. Agricultural fertilizer escapes

from fields through both air and water, enhancing the growth of wild plants downwind and downstream. An even bigger contribution to global nitrogen fertilization is the production of NO and NO₂ by combustion in engines and industry. This “burned air” further oxidizes to NO₃ when dissolved in cloud droplets and falls as dilute inorganic fertilizer in rain and snow for thousands of km downwind. Regional air pollution hotspots like the US Midwest, Western Europe, and East Asia are located upwind of major forests whose carbon–nitrogen ratios are greater than 100:1, meaning that each kilogram of reactive N may stimulate the sequestration of 100 kg of C. Nitrogen deposition and elevated CO₂ may cofertilize such forests, and indeed, the FACE studies described earlier have shown that adding N often reaccelerates plant growth under enhanced CO₂.

When European settlers arrived in the New World, they began transforming high-carbon forests into lower-carbon farms and pastures, converting wood and soil carbon into CO₂. In the 20th century, widespread deforestation migrated to the tropical ecosystems of the developing world. Even now, tropical deforestation accounts for perhaps 1 GtC year⁻¹ of CO₂ emissions, about a tenth of the rate of emissions from fossil-fuel combustion. In the developed world, by contrast, agriculture has become much more centralized in highly productive regions and millions of smallholder farms have been allowed to grow back into woodland and forest as people migrated to suburbs and cities. Reforestation may be the dominant carbon sink in the eastern United States, and in parts of Europe, Japan, and Australia. Other changes in land use such as forest fire suppression and heavy grazing of grasslands also lead to accumulation of carbon at regional scales.

A final important terrestrial carbon sink mechanism is associated with the very rapid warming of the northernmost land. Arctic amplification of global warming has led to boreal growing seasons that are 50% longer than they were a few decades ago. Warmer soils allow decomposition to free more nutrients from organic matter, and the steady encroachment of trees and shrubs into tundra regions allows carbon to accumulate in these landscapes. The boreal and arctic regions are much less productive than tropical forests, but they cover a very large area and their greening has been well documented by satellite imagery collected since the 1970s.

Carbon Sinks and Climate Change

It is very fortunate that chemical and biological processes in both oceans and land each sequester about 25% of global fossil-fuel emissions, because this means that atmospheric CO₂ is increasing only about half as fast as it would be without these sink processes. As we saw in the section “How Sensitive Is the Earth’s Climate to Changes in CO₂?” meeting the international target of limiting eventual global warming to 2°C will require limiting CO₂ to about 455 ppm, which only allows for about 100 additional GtC added to the atmosphere. This would only take about 10 years at the current rate of global fossil-fuel emissions (10 GtC year⁻¹), but land and ocean carbon sinks act as an effective emissions reduction of 50%. If these sink processes continue as they have been, it will take about 20 years to burn through the remaining 100 GtC “budget” of the atmosphere at current emissions rates (Meinshausen et al., 2009). Of course, reducing emissions would buy us more time, increasing emissions would lose time, and a large change in the behavior of land and ocean carbon sinks might change these calculations quite a lot.

What Will Happen to Carbon Sinks in Coming Decades?

The global ocean carbon sink depends primarily on the chemistry of dissolved CO₂ (see Box 1), the formation of cold deep waters in the polar regions (the solubility pump), and the productivity of marine ecosystems (the biological pump). Over periods of a few decades, these are unlikely to stop working, though there is some reason for concern. As sea surface temperatures warm, polar waters become more buoyant and may not carry dissolved CO₂ as readily into the deep ocean. Most numerical climate models predict that the solubility pump will eventually slow due to surface warming, but probably not until the late 21st century at least.

A more pressing concern is that loading the surface ocean with carbonic acid through fossil-fuel emissions acidifies the water. Ocean pH drops as hydrogen ion becomes concentrated through the dissociation of carbonic acid and bicarbonate ion. Given the current chemical state of the ocean, each molecule of added CO₂ consumes a carbonate ion (CO₃²⁻) to add bicarbonate to the water column. Many marine organisms make hard body parts from calcium carbonate (CaCO₃), so depletion of CO₃²⁻ increases their solubility. Long before ocean waters become caustic to seashells and coral reefs, these organisms would starve because of the additional energy required to extract diminishing carbonate from seawater. This may in turn impact the biological carbon pump because calcium carbonate serves as “ballast” for a lot of sinking carbon.

On land, the situation is more urgent. Only CO₂ fertilization is likely to grow in strength as a carbon sink over time. All the other terrestrial sink mechanisms are nearly certain to saturate over a period of decades, after which CO₂ will rise more quickly. As anybody knows who has tended a lawn or garden, adding nitrogen to plants makes them grow faster, but adding twice as much does not make them grow twice as fast. Once nitrogen demand has been met, further additions will simply run off or leach out. Too much excess nitrogen is even likely to injure or kill the plant. Sinks due to changing land use are also transient. Before the year 1700, the concentration of atmospheric CO₂ was remarkably steady for many millennia because growth and death were balanced. Regrowing forests on abandoned farms sequester carbon because pools of organic matter are still small relative to the rate of growth. Conversely, harvesting old forests replaces a landscape with high carbon density with much smaller pools, which releases CO₂ to the atmosphere. As they mature, carbon accumulates until the rate of death and decomposition balances the rate of growth. Forest fire suppression only allows carbon to build up until the next big fire. Land carbon sinks due to boreal warming are the most fickle of all; a little warming may allow woody encroachment into tundra, but a lot of warming may thaw the permafrost, allowing thousands of years’ worth of stored carbon to decompose like frozen food when the freezer breaks down.

Scientists have argued for decades about the relative contributions of CO₂ fertilization, nitrogen fertilization, changing land use, and boreal warming to terrestrial carbon sequestration. If most of the land sink in recent decades is driven by CO₂ itself, then the land sink is likely to persist or even increase with atmospheric CO₂. On the other hand, if the sink is dominated by nitrogen deposition, regrowing forests, and the greening north then it is quite likely to shut down.

Climate change may also impact carbon sequestration more directly. Land ecosystems require more water when temperatures rise, so that drought stress increases even if rain and snow hold steady. Higher CO₂ levels mitigate some of this increased evaporative demand because plants can use water more efficiently when they can absorb more CO₂ without opening the pores in their leaves as much. Global warming is also changing atmospheric circulation, so that rainfall patterns shift. Nearly all climate models project declining precipitation in the southwest United States, southern Europe, the Middle East, and parts of Asia. Many models also suggest progressive drying of the Amazon basin. Increased drought stress in these regions is likely to reduce carbon storage. Warmer climates are also associated with enhanced microbial decomposition, further impacting carbon pools and raising atmospheric CO₂ rather than mitigating it as land carbon sinks become sources.

The Long-Term Fate of CO₂ From Fossil-Fuel Combustion?

After people stop burning fossil fuels, it will take many centuries or even millennia for atmospheric CO₂ concentrations to return to preindustrial levels (Archer et al., 2009). Land carbon sinks will be important controls on the rate of CO₂ increase and climate change over the next few decades, but the ultimate capacity of terrestrial ecosystems to store anthropogenic carbon is limited by the relatively small fraction of the Earth's surface that is well watered and fertile. If human society burns past our carbon budget and dumps many hundreds of GtC into the atmosphere, land carbon sinks will be completely saturated. Severe climate change could easily turn the land into a strong source of CO₂.

Long after land ecosystems have equilibrated with higher levels of CO₂ and a new climate, the oceans will continue taking up anthropogenic CO₂. The rate of net carbon uptake by the oceans depends on the rate of physical mixing between the warm and buoyant surface and the cold and dense deep waters beneath. This is principally driven by the formation of extremely cold water at the surface in the polar winter, but it takes about 1000 years for this "deepwater formation" mechanism to bring the whole mass of the ocean into contact with the atmosphere once. Each millennial ocean overturning will allow ocean waters to more closely approach chemical equilibrium with atmospheric CO₂, but this will remove CO₂ from the air much more slowly than the oceans do now.

Ocean acidification and progressive depletion of carbonate ion in the first 3000 years or so after fossil-fuel emissions cease will reduce the oceans' capacity to absorb CO₂ from the atmosphere. The degree of acidification depends on the total amount of fossil fuels our descendants ever burn. If China, India, and Africa build industrial economies based on fossil fuels in this century, ocean acidification may eventually cause mass extinction of most species that make body parts out of calcium carbonate. This would also leave about 20% of the anthropogenic CO₂ in the atmosphere 10,000 years after the end of fossil-fuel combustion.

Once land ecosystems and the oceans have equilibrated with anthropogenic CO₂, geologic processes will accomplish removal of the remaining carbon from the atmosphere. Chemical weathering of rocks slowly consumes atmospheric CO₂. The rate of this geologic sequestration depends on exposure of fresh (unweathered) rock by erosion and mountain building.

The last time atmospheric CO₂ spiked by several hundred percent (about 55 million years ago), ocean chemistry and chemical weathering eventually absorbed the excess, but the process took about 200,000 years. If modern society repeats this experiment, a similar result is likely.

How Can Carbon-Climate Science Help Inform Policy?

As we have seen, a thorough understanding and accounting of the contemporary carbon budget is critical for relating fossil-fuel emissions to atmospheric CO₂ and therefore climate. Only about half of fossil-fuel emissions are currently accumulating in the atmosphere. The other half is being sequestered by strong net sink processes in both the oceans and land ecosystems. These land and ocean carbon sinks involve perturbations of just a few percent of the natural two-way exchanges with these reservoirs, and they have persisted for decades.

On decadal timescales relevant for policy, ocean carbon sinks are more reliable than those on land. If carbon sinks continue to sequester 50% of fossil-fuel emissions, then the global economy can burn perhaps another 200 GtC without crossing the agreed-upon 2°C warming threshold. This would take only 20 years at current emission levels—less if global emissions rise, longer if emissions are reduced. If land sinks saturate quickly, the total "carbon budget" will be reduced as a result.

To the extent that terrestrial sinks are driven by CO₂ fertilization, they are likely to persist and even strengthen in coming decades. This would buy time for human societies, but it is by no means a sure thing. To the extent that nitrogen deposition, changing land use, and boreal warming/greening drive the contemporary sink, it is very vulnerable. It is therefore important for science to quantify the contributions of various mechanisms to the land carbon sink. This has been the subject of a major international effort for decades. Scientists measure the carbon stored in trees and soils, count tree rings to measure changing growth rates, and calculate rates of deforestation and reforestation from satellite imagery. They use "eddy covariance" on tall towers to relate CO₂ concentrations in updrafts and downdrafts over hundreds of ecosystems and build FACE rings in forests, grasslands, and deserts. They even

measure atmospheric CO₂ from space at hundreds of thousands of locations each day to detect source and sink regions from tiny variations in gas concentration.

A quantitative accounting of past carbon sinks is necessary but not sufficient for the development of predictive models of the fate of atmospheric CO₂ in the future. Such predictive models are needed to relate CO₂ emissions to concentration and climate and are therefore valuable policy tools. Carbon models predict photosynthesis, plant growth, carbon allocation, mortality, disturbance, and recovery on land. Ocean carbon models predict air–sea gas exchange, marine biology and chemistry, and the effects of solubility and circulation. These models are then coupled to the atmosphere to predict the tiny variations in CO₂ observed by satellites, aircraft, and ground-based instruments.

Future carbon sources and sinks also depend on the interaction of physical climate with biological systems. Changes in sea surface temperature and ocean mixing may reduce the rate of ocean carbon uptake. Changes in temperature, atmospheric circulation, and rainfall may also degrade the capacity of land ecosystems to store carbon. Either of these outcomes would increase the amount of carbon in the atmosphere and amplify global warming. It is critical that scientists understand and improve our predictive models of these feedbacks between physical climate and the carbon cycle. Because we cannot adequately quantify carbon–climate feedbacks, the current generation of models used by the IPCC disagrees by almost 350 ppm on the atmospheric CO₂ concentration in 2100 for the same high-emission scenario (Hoffman et al., 2014).

Developing sound policy depends on the ability to project the consequences of decisions regarding fossil-fuel emissions. These in turn depend on a quantitative and predictive understanding of both climate sensitivity and the interactions among physical climate, atmospheric CO₂, and the global carbon cycle.

See also: [Energy and Natural Resources](#); [Environmental Change and Energy](#); [Overview Article for the Geologic History Section](#).

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Relevant Websites

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