

Chapter 10. The Perturbed Carbon Cycle

Abstract

We describe three geochemical global change issues here. Ozone in the stratosphere is beneficial because it shields us from ultraviolet sunlight, but it is depleted by chlorofluorocarbons. Ozone in the troposphere is harmful to lungs and to plants, but it is produced by automobile emissions. Neither problem has much to do with global warming but we present it to allay confusion about this.

Methane is produced by livestock and rice paddies as well as natural sources. The lifetime of methane in the atmosphere is about 8 years. The concentration of methane in the atmosphere can be calculated from the source flux multiplied by the lifetime.

CO₂ is accumulating more slowly in the atmosphere than we are releasing it, because of natural uptake by the terrestrial biosphere and the ocean. Ocean uptake is easier to quantify than terrestrial, because chemical properties in the ocean are less patchy than they are on land. CO₂ has a long lifetime in the atmosphere, and will influence the climate for hundreds of thousands of years into the future. Long-term projections of carbon use, compared with the demands of stabilizing the CO₂ concentration of the atmosphere, indicate that a major new source of carbon-free energy will be required in the coming century, with the capacity to produce as much energy as we are currently consuming or even more.

Ozone

Let's get one issue out in the open and out of the way before we begin thinking about global warming. The ozone hole is not the same as global warming. **Ozone** is a reactive oxygen molecule comprised of three oxygen atoms. Ozone in the stratosphere is produced as O₂ molecules are zapped by energetic UV-C ultraviolet light, breaking apart into two very reactive oxygen atoms. Each of these may find another O₂ molecule and join it, to form O₃, ozone. Ozone itself absorbs UV light called UV-B that is less energetic but more abundant than the UV-C required to break up an O₂ molecule. Stratospheric ozone filters UV-B radiation that might otherwise reach the surface, causing skin cancers and sunburn.

Atmospheric chemists predicted that ozone concentrations in the stratosphere might be depleted by chemical reactions accompanying the breakdown of chemicals called chlorofluorocarbons or Freons, inert chlorine-bearing compounds that are used in refrigerators and air conditioners. The prediction was that stratospheric ozone concentrations would gradually decrease over decades. This has been observed, but what scientists did not anticipate was a surprise called the **ozone hole**. The ozone hole is located in the Southern hemisphere over Antarctica. In winter time in this region, it gets cold enough that an unusual form of cloud forms in the stratosphere, comprised of frozen particles of nitric acid, HNO₃. It turns out that the frozen nitric acid clouds convert the chlorine from breakdown of freons into a very reactive form that doesn't just deplete

ozone by a small amount, but consumes it entirely within that air mass. The ozone hole was first observed in measurements of ozone concentration made by hand, on the ground. After these measurements, old satellite ozone records were examined, and it turned out that the satellite had been seeing the ozone hole for several years, but a data quality algorithm had been programmed to throw out any data which violated common sense, and out with the bad data went the ozone hole. This is a measure of how much of a surprise it was.

The ozone hole is a terrific example of a **smoking gun**, clear-cut proof of the detrimental effects of chlorofluorocarbons on stratospheric ozone. Before the ozone hole was detected, the models predicted a gradual decrease in stratospheric ozone globally, superimposed on natural variability; a difficult prediction to prove. As a result of the ozone hole, and the availability of economically and technologically viable alternatives, many countries of the world ratified the Montreal Protocol in 1987, phasing out further production and release of chlorofluorocarbons to the environment.

Ozone is also produced by reaction of gases from industrial activity, mostly automobile exhaust, in surface urban smog. The ingredients for ozone production in urban air are evaporated organic carbon compounds, like evaporated gasoline or molecules that are emitted naturally from trees and plants, nitrogen oxide compounds that are emitted from automobiles, and sunlight. When ozone concentrations exceed a toxic limit, asthma sufferers begin to feel discomfort, and plant leaves get “burned” and scarred.

Ozone in the stratosphere interacts with climate change caused by greenhouse gases such as CO₂. The main role that ozone plays in the energy budget of stratospheric air is it absorbs ultraviolet light from the sun, heating up the air. Ozone is the reason why there is a stratosphere. If ozone did not heat up the stratosphere, the atmosphere would continue to get colder with altitude as it does in the troposphere. The stratosphere would disappear into the troposphere. Decreasing ozone results in less heating, and cooler air in the stratosphere.

Rising CO₂ concentrations also cool the stratosphere. The role that CO₂ plays in the heat balance of stratospheric air is that it acts like a radiator fin, exporting heat energy as infrared light. For this reason, an increase in CO₂ concentration in stratospheric air causes the temperature there to go down. Ozone is also a greenhouse gas, but ozone has a stronger influence on the heat balance by absorbing UV.

So we have stratospheric cooling for two reasons: falling ozone concentration and rising CO₂. Now the thread of the story makes its way back to ozone. The stratospheric clouds that cause the ozone wipe-out in the ozone hole are more prevalent when the air is cold. They are clouds of nitric acid ice, which only form in extremely cold air. Decreasing ozone leads to decreasing stratospheric temperature, leads to further ozone depletion. This is an example of positive feedback.

Ozone is confusing to the student of the environment because ozone in the stratosphere is a good thing but industrial activity is acting to deplete it, while ozone in the troposphere is a bad thing and industrial activity tends to produce it.

Methane

Methane is a greenhouse gas, 20 times more powerful per molecule than CO₂ at current concentrations (see [Chapter 4](#)). Methane has natural sources as well as additional anthropogenic sources to the atmosphere ([Table 10-1](#)). Once released to the atmosphere, methane reacts slowly with activated oxygen compounds to oxidize back to CO₂. The reactive oxygen compounds are produced by sunlight. In the absence of sunlight methane and O₂ gas coexist in ice core bubbles for hundreds of thousands of years with no reaction. Put it in the sunlight and it slowly burns up.

The rate of methane emission, and the atmospheric lifetime of methane, together determine the concentration of methane in the atmosphere. Let's assume that the methane release rate is steady from one year to the next for a long time. Let's also assume that the emission of methane must be balanced by the rate of methane decomposition. The fluxes balance exactly if the methane concentration were constant with time. As it is, methane is rising with time, so our steady-state assumption is not strictly correct, but it is close enough to be useful. The steady-state assumption is

$$\text{emission [Gton C / year]} = \text{decomposition [Gton C / year]}$$

The lifetime of a methane molecule in the present-day atmosphere is about 8 years. Methane is consumed by reactive oxygen compounds in the atmosphere, in particular a molecule called OH radical. OH radical is related to ozone, so one could imagine a change in OH radical driven by the change in ozone chemistry of the atmosphere. It could be that if the methane concentration were higher, the lifetime might be longer, because degradation might be limited by the availability of OH radical molecules. If however we toss out these potential complications, and just assume that the atmospheric lifetime of methane is and will always be 8 years, we could just write that the degradation rate of methane is

$$\text{decomposition [Gton C / year]} = \text{inventory [Gton C]} / \text{lifetime [years]}$$

Combining these two equations, we get

$$\text{emission [Gton C / year]} = \text{inventory [Gton C]} / \text{lifetime [years]}$$

Rearranging,

$$\text{inventory [Gton C]} = \text{CH}_4 \text{ emission [Gton C / year]} * \text{lifetime [years]}$$

This relation tells us that the methane concentration in the atmosphere is linearly related to the methane source to the atmosphere, as long as the lifetime of methane stays the same. If we doubled the emission, after a few decades, the steady-state concentration

would double. The real world may be a bit more complicated, because the lifetime may change as the methane concentration goes up.

One of the natural sources of methane to the atmosphere is the degradation of organic carbon in freshwater swamps. Organic carbon degrades first by reaction with O_2 , as we have discussed in [Chapter 8](#). In seawater, after the O_2 is gone, organic carbon reacts with sulfate ion, SO_4^{2-} , to produce hydrogen sulfide, H_2S . After oxygen and sulfate are depleted, methane is produced from organic carbon by fermentation. This is how the methane is produced that freezes into clathrate deposits below the sea floor.

In fresh water, there is not much SO_4^{2-} , so as soon as oxygen is gone, methane production begins. Methane is found much shallower in fresh water mud than in salt water mud. If you step in mucky swampy freshwater mud you may see bubbles of methane rising up around your legs. Methane is sometimes referred to as swamp gas for this reason, and is one of the usual suspects blamed for UFO sightings. Bubbles of ancient atmosphere preserved in ice cores tell us that the methane concentration has fluctuated with climate state over the past 400,000 years (the longest ice core yet available), with lower methane concentrations during colder, drier climate stages ([Figure 8-3](#)). This is interpreted to be the result of the changing abundance of swamps.

Anthropogenic sources of methane include production in the guts of ruminant animals, and release as leakage by the fossil fuel industry. Rice paddies often provide ideal anoxic freshwater environments for methane production. The methane concentration has doubled over its pre-anthropogenic concentration ([Figure 10-1](#)), and is responsible for a quarter of anthropogenic greenhouse heat trapping ([Figure 10-2](#)).

CO_2

There are two main anthropogenic sources of CO_2 to the atmosphere. One is deforestation. A heavily-wooded forest holds more carbon per area than does a plowed agricultural field. The world's forests started to feel the ax thousands of years ago with the development of agriculture and the growing of the human population. Most of the temperate latitudes have been cut long since, and the tropics are currently being cut. The year 1750 has been taken as the beginning of the anthropogenic CO_2 rise, although it has been argued that both CO_2 and methane may have started rising from their "natural" trajectories thousands of years ago. The rise in atmospheric CO_2 after 1750 ([Figure 10-1](#)) is clearly the result of deforestation, perhaps in the New World (the "pioneer effect"). Today, visible deforestation is mostly to be found in the tropics, and accounts for about 2 Gton C / yr release of CO_2 to the atmosphere.

The other main anthropogenic CO_2 source is of course the combustion of fossil fuels discussed in the last chapter. Fossil fuel combustion releases 5 Gton C / yr, rising exponentially, driven by population growth and economic growth, rising in spite of increases in energy and carbon fuel efficiency.

Combining the ocean and tropical deforestation, mankind is releasing carbon to the atmosphere at a rate of about 7 Gton C / yr. The atmospheric CO_2 inventory is rising at a

rate of about 3 Gton C / yr. Where is the other 4 Gton C / yr? There are two main natural sinks for CO₂ that are operating today; one is the oceans, and the other is the terrestrial biosphere.

Carbon uptake by the terrestrial biosphere on land, the **terrestrial carbon sink**, is difficult to measure. In comparison with the ocean, the distribution of carbon on land is very spotty. Recall from **Chapter 7** that most of the carbon on land is in the soil, rather than in the trees where we could see it. In soils, the amount of carbon depends on the recent history of the land: fires, agriculture, erosion, and so on. It is difficult to know precisely how much carbon there is on land because the measurements are so variable; you would have to make a lot measurements in order to average out all the noise of natural variations. As a result of this, it would be possible to increase the amount of carbon on land, a little bit here or there, in a way that would be entirely invisible to direct measurements. The land is playing two roles in the carbon budget story, one as visible deforestation source and another as a potential invisible carbon uptake sink.

One way to estimate the invisible terrestrial uptake is by putting together the rest of the carbon budget and assign the terrestrial biosphere whatever is left over. The chemical properties of seawater vary more smoothly than they do on land, so our estimates of ocean uptake are better than they are for the land. Another is to measure CO₂ concentrations in the atmosphere, in the winds as they blow across the land, to see if CO₂ is going into or coming out of a given forest. This doesn't sound easy, but it can be done. There is a network of "CO₂ observatories" around the globe, where precise CO₂ concentration measurements are made daily, for uses such as this.

There are several reasons why the land may be willing to take up CO₂ as the atmospheric CO₂ concentration rises. One is that with warming, there will be a longer growing season. This has been observed in many climate and botanical records. With warming, some tundra areas become amenable to conquest by forests. Rising CO₂ in the atmosphere may also directly encourage plants to grow faster, by a process known as **CO₂ fertilization**. Plants run their photosynthetic machinery inside waxy walls on the surfaces of leaves. Gases are exchanged with the outside atmosphere through adjustable vents called **stomata**. When the leaf needs CO₂ for photosynthesis, the stomata open. The cost of opening stomata, though, is loss of water. So if CO₂ concentrations were higher in the outside atmosphere, plants could get the CO₂ they need without opening their stomata as much or as often. They could therefore be stingier with their water. There is no doubt that this is a real effect; CO₂ concentrations in greenhouses are typically higher than in the outside atmosphere, one of the ways that greenhouses are good for plants. However, in the real world, plant growth is very often limited by something else other than water stress, such as fertilizers like nitrogen or phosphorus. Scientists do CO₂ fertilization experiments in natural settings by pumping CO₂ continuously into the air. When the wind changes, they adjust the location of the CO₂ vent, so that the target grove is always downwind from a CO₂ source. These experiments go on for years! What they tend to find is initial growth spurt from CO₂ fertilization, followed by a leveling off at something like the initial rates.

There is another process that may affect CO₂ storage on land, which is a temperature sensitivity to respiration, the process that converts soil organic carbon back into CO₂. Soil respiration really gets going as it gets warmer. Think of a ham sandwich, half of which is safely stowed in the refrigerator while the other half sits on a plate in the sun. Which half will stay tasty longer? For this reason, there is very little organic matter in tropical soils, while high latitudes may host peat deposits that contain prodigious carbon deposits for thousands of years. Warming and melting and decomposition of high-latitude permafrost may contribute CO₂ to the atmosphere.

Uptake of fossil fuel CO₂ by the oceans is called the **ocean carbon sink**. The ocean sink depends on ocean circulation, and on the chemical forms that dissolved CO₂ takes in seawater. The ocean covers 70% of the earth's surface, and the length and width of the ocean are huge compared with its depth, which averages about 4 km. The deep ocean is so close to the surface, and yet it is so very far away. The way the ocean circulates, the deep ocean is very cold, and the only place where surface waters are cold enough to mix with the deep ocean is in high latitudes. The ocean surface is huge, but the deep ocean, which is the largest water type in the ocean, only sees the atmosphere through a very small area of sea surface.

The densest water at the sea surface is in the Antarctic and in the North Atlantic, because it is cold there. Surface waters from these locations sink to the deep ocean, filling up the entire deep ocean like a bucket with cold polar water that is only a few degrees warmer than freezing. The cold deep ocean fills up until cold polar waters underlie the warm surface waters in lower latitudes. The warmer waters mix with the cooler, eroding the cold water and making room for more of the coldest water to continue filling the deep sea. As new cold water flows from the high-latitude surface ocean into the abyss, it carries with it atmospheric gases like anthropogenic CO₂, a process known as **ocean ventilation**. It takes centuries for the waters of the deep ocean to travel through this cycle. For this reason, the time scale for getting anthropogenic CO₂ into the deep ocean is centuries.

The shallower ocean has other water masses and circulation modes that are wondrous to learn about and study if one is of a mind to. The zone of the ocean separating the warm from the cold is called the **thermocline**. Thermocline waters may be exposed to the atmosphere in winter, when the sea surface waters are cold. Once a parcel of thermocline water becomes isolated from the sea surface, it follows a trajectory determined by its density and by the rotation of the earth. Thermocline waters ventilate to the atmosphere on a time scale of decades.

The surface ocean water mass is not as large as the deep sea or the thermocline, but it is a respectable carbon reservoir of its own. Turbulence generated by the wind acts to mix the surface ocean down to a typical depth of 100 m. For most gases, this surface ocean layer 100 meters thick would equilibrate with the atmosphere in about a month.

CO₂ differs from other gases, however, in that it has chemical equilibrium reactions with water and hydrogen ions. Hydrogen ions are very reactive. If a solution has a high concentration of hydrogen ions, we call it **acidic**. A strongly acidic solution, such as

battery acid for example, can burn your skin or clothes by chemical reaction with hydrogen ions. The acidity of a solution is described by a number called the **pH** of the solution, which can be calculated as

$$\text{pH} = -\log_{10} [\text{H}^+]$$

The \log_{10} is the base-10 logarithm, meaning that if $x = 10^y$, then $\log_{10} x = y$. The hydrogen ion concentration is denoted by the square brackets, and is expressed in units of moles of H^+ per liter of solution. A **mole** is simply a set number of atoms or molecules, called Avagadro's number and equal to $6.023 \cdot 10^{23}$. The hydrogen ion concentration in seawater usually ranges from 10^{-7} to $10^{-8.3}$ moles of H^+ per liter. The pH of seawater therefore ranges from 7 to 8.3. Note that the more acidic the solution, the lower the pH of the solution. Ads for shampoo used to claim "low pH" as though pH were some toxic ingredient. I guess it sounded better than calling the shampoo "strongly acidic".

When CO_2 dissolves in water, it reacts with water to form **carbonic acid**, H_2CO_3 .



Carbonic acid loses a hydrogen ion (that's what acids do, in general, is release hydrogen ions) to form **bicarbonate ion**, HCO_3^-



A second hydrogen ion can be released to form **carbonate ion**, $\text{CO}_3^{=}$

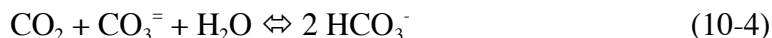


The concentrations of carbonic acid, bicarbonate, and carbonate ions control the acidity of the ocean, just as they control the acidity of our blood and cell plasma.

These chemical reactions are fast enough that the distribution of chemical species will always be in their lowest-energy distribution. Many chemical reactions that we will encounter will not be in equilibrium, so we should enjoy this equilibrium system while we have it. Equilibrium reactions can be easily and very precisely predicted. In a qualitative way, we can use an idea known as **le Chatelier's principle** to take a stab at the behavior of an equilibrium system. Le Chatelier's principle states that an addition or removal of a chemical on one side of the chemical equilibrium will cause the reaction to run in the direction to compensate for that change. Take some of something out, the equilibrium will put some of the something back. Add more something, the equilibrium will remove some of the something.

Le Chatelier's principle is treacherous for students of the carbon system in seawater, though, because we have an innate human tendency, I have found, to ignore the hydrogen ions. They are such tiny things, after all. There are far fewer hydrogen ions in seawater than there are of the dissolved carbon species. What this means, however, is that a small change in the concentrations of the carbonate species might make a huge change in the

hydrogen ion concentration. The safest assumption to make is that the carbon species have to get along together without counting on sloughing off too many hydrogen ions at all. Hydrogen ion is such a tiny slush fund, it might as well not exist. We can combine reactions 10-1, 10-2, and 10-3 into a single reaction, in such a way that we don't allow any production or consumption of hydrogen ions



To this reaction we can apply Le Chatelier with impunity. If we were to add CO_2 to this system, the equilibrium would compensate somewhat by shifting to the right, consuming some of the CO_2 by reacting it with $\text{CO}_3^{=}$.

Seawater has the capacity to absorb or release more CO_2 than it would if CO_2 had no pH chemistry, because of the other carbon reservoirs HCO_3^- and $\text{CO}_3^{=}$. It is like sitting at a poker game, with a rich uncle sitting behind you covering most of your losses and taking splits of your winnings. The pH reactions of H_2CO_3 , HCO_3^- , and $\text{CO}_3^{=}$ are called a **buffer**, because any changes to the chemistry tend to be resisted or buffered by the chemical reactions. The CO_2 concentration of seawater is buffered by its pH chemistry. Another way of saying this is that the seawater has greater capacity to hold seawater than it would if CO_2 were not buffered.

The strength of the buffer is about a factor of 10, meaning that seawater has a capacity to hold 10 times as much CO_2 as it would if there were no buffer chemistry. The factor of 10 comes from the fact that there is about 10 times more $\text{CO}_3^{=}$ than dissolved CO_2 in surface ocean water. Carbonate ion is our anti- CO_2 , reacting with new CO_2 , hiding it away as bicarbonate; this is the action of the buffer.

As the CO_2 concentration in the atmosphere increases, and CO_2 invades the ocean, the concentration of carbonate ion goes down, according to the equilibrium chemical reaction 10-4. As the carbonate ion becomes depleted, so is its ability to buffer CO_2 . Ocean uptake of new CO_2 would decrease as a result of this. The future of ocean uptake of fossil fuel CO_2 may also be affected by changes in the circulation of the ocean. Surface warming is expected to be most intense in high latitudes because of the ice-albedo feedback (Chapter 7). If the high latitudes warm, the overall circulation of the subsurface ocean may decrease. The circulation of the ocean may stagnate, slowing uptake of CO_2 .

Biology in the ocean acts to decrease the CO_2 concentration of surface waters, by converting CO_2 into organic carbon via photosynthesis (Chapter 8). Dead phytoplankton sink from surface waters, exporting their carbon to the deep sea. This process has been termed the **biological pump**. If all the life in the ocean were killed, that is if the biological pump were stopped, then the CO_2 concentration of the atmosphere would rise. If the biological pump were stimulated to work harder, it could decrease the CO_2 concentration of the atmosphere. One proposal for dealing with global warming is to fertilize the ocean with iron. Iron concentrations are extremely low in remote parts of the ocean, far away from iron deposition from dust and iron bleeding from surface sediments. Supplying iron to the phytoplankton has been shown to stimulate phytoplankton growth in the Southern Ocean around Antarctica for example. The problem is that it takes

hundreds of years for the ocean and the atmosphere to negotiate what the atmospheric CO₂ concentration should be; it's slow, recall, because the ocean circulation is so slow. Model studies have shown that fertilizing the Southern Ocean for hundreds of years might bring the CO₂ concentration of the atmosphere down, but fertilizing for a few decades has very little impact.

Decreasing carbonate ion may also be detrimental to coral reef and other organisms that produce limestone, CaCO₃, from calcium ion, Ca²⁺, and carbonate ion. It's like pouring vinegar on limestone steps; you will see bubbles as the acid of the vinegar converts the CaCO₃ to CO₂. Fossil fuel CO₂ is itself an acid, and drives CaCO₃ to dissolve. Note the counter-intuitive reverse behavior; one might have thought that adding CO₂ to the oceans would lead to an increase in the amount of carbon that winds up as CaCO₃. The response is opposite this expectation because CO₂ is an acid and CaCO₃ reacts with acid. Fish and other aquatic organisms also react poorly to the acidity and higher CO₂ concentrations resulting from fossil fuel CO₂ release. This danger is called the **acid ocean**.

Uptake of CO₂ into the oceans has been estimated by a number of different independent methods. These include measurements of the chemical concentrations throughout the world ocean, and modeling the circulation and carbon cycle. Other chemicals serve as tracers for how the ocean circulates. These include radioactive elements produced naturally by cosmic rays, or in nuclear bomb tests in the 1960's, and industrial chemicals like chlorofluorocarbons. Another distinction between dissolution of CO₂ in the ocean versus uptake of CO₂ by photosynthesis on land is that photosynthesis releases oxygen, while dissolution in water does not. So you can measure the change in CO₂ and O₂ in the atmosphere to figure out what fraction of the missing CO₂ is going into the ocean versus into the terrestrial biosphere by photosynthesis.

There are discrepancies between the different estimates of ocean and land carbon uptake, and uncertainties associated with each method, but in general they all point to about a 50:50 split. The ocean gets about 2 Gton C per year of the anthropogenic CO₂ and the terrestrial biosphere gets 2 Gton C per year. The terrestrial uptake of new CO₂ is thought to be taking place in high northern latitudes, perhaps into the great forests of Canada and Siberia.

What about carbon uptake by the natural world in the future? It is certainly possible that the land carbon reservoir will change in the coming centuries, depending on how people decide to use the land surface, in addition to biological factors such as CO₂ fertilization and increases in soil respiration. So far, the amount of carbon released, about 300 Gton C, is smaller than the size of the terrestrial biosphere (500 Gton C), especially if we consider soil carbon (1500 Gton C). It is reasonable to think about the land surface as a potential major player in the carbon budget. However, if we combust all of the coal or methane clathrate deposits, the amount of CO₂ we could release could be 5000 Gton C or more, several times larger than the carbon stored on land. It would be difficult to imagine the terrestrial biosphere saving the day in that case.

After hundreds of years, about 75% of the fossil fuel CO₂ will dissolve in the oceans, while the remaining 25% remains in the atmosphere, awaiting slow chemical reactions with rocks that will ultimately consume it (Figure 10-3). The CO₂ invasion lowers the pH of the ocean and the concentration of carbonate ion. On time scales of thousands of years, the pH and carbonate ion concentration of the ocean are controlled by limestone, CaCO₃. Limestone on land dissolves, a chemical reaction we have already defined as weathering. Dissolved limestone flows to the ocean in rivers. Plankton re-form the solid limestone to make shells of CaCO₃, some of which sink to the sea floor and are buried.

The effect of the CO₂ invasion of the ocean will be to make it harder for little shells to be buried. In fact, if we ultimately release 1000 Gton C or so, there will be net dissolution of CaCO₃ from the sea floor. Mankind will have reversed the net sedimentation of the ocean! Engineers in Chicago early in the last century reversed the flow direction of the Chicago River. That was impressive in its time, but it was nothing compared to this. The rate of CaCO₃ weathering will exceed CaCO₃ burial, and so dissolved CaCO₃ will accumulate in the ocean. The fossil fuel CO₂ acts as an acid, lowering the pH of the ocean, while the dissolved CaCO₃ is a base, pushing ocean pH back up toward its natural value. Restoring the pH of the ocean will draw down the atmospheric CO₂ somewhat. This process will take thousands of years.

On time scales of hundreds of thousands of years, the silicate weathering thermostat, defined and described in Chapter 7, will act to pull CO₂ down the rest of the way toward the pre-anthropogenic value. The bottom line is that about 15-30% of the CO₂ released by burning fossil fuel will still be in the atmosphere in 1000 years, and 7% will remain after 100,000 years. Truly, global warming is forever.

Of the 7 Gton C / yr that mankind is releasing to the atmosphere today, 4 Gton C / yr is going away as quickly as we release it. This leads to a simple but powerful conclusion: if we want atmospheric CO₂ to stop going up, tomorrow, we have to reduce our CO₂ emissions from 7 Gton C / yr down to 4 Gton C / yr, say a reduction of total carbon emission by 40%. Then the CO₂ concentration in the atmosphere would stop rising, but remain at its current level of 365 ppm. This could continue until the terrestrial biosphere and the ocean equilibrated at this new level, “filled up” with the new higher CO₂. No one has any idea how long it would take for the terrestrial biosphere to saturate or fill up, but the ocean would take several centuries. If emissions were stopped after that, the atmospheric CO₂ concentration would remain at 365 ppm for thousands of years.

The aim of the Kyoto Protocol, the international agreement to reduce CO₂ emissions discussed in Chapter 13, is to reduce emissions to about 6% below the 1990 levels, resulting in emissions that are still very close to 7 Gton C / year. CO₂ emissions under business-as-usual are projected to grow, so the rather modest-sounding 6%-below-1990 target actually amounts to about 30% reductions from the projected 2010 rate. Still, this is just a drop in the bucket of what would be required to truly stabilize the CO₂ concentration of the atmosphere. The Kyoto protocol by itself is not sufficient to end the problem of global warming; it can only be the first step, alas.

Take-homes

The ozone hole is not global warming. They are different issues.

Methane has a short lifetime in the atmosphere.

CO₂ has a long lifetime in the atmosphere. Stabilizing CO₂ in the atmosphere at some "safe level" (whatever that is) will require major new energy initiatives.

Further Reading

Online Trends, a Compendium of Data of Global Change, from the Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.
<http://cdiac.esd.ornl.gov/trends/trends.htm>

The Discovery of Global Warming (2003) by Spencer Weart. The history book again. Read about early measurements of atmospheric CO₂.

IPCC Scientific Assessment 2001, from Cambridge University Press or downloadable from http://www.grida.no/climate/ipcc_tar/. Chapter 3 **The Carbon Cycle and Atmospheric Carbon Dioxide**.

Archer, D., Fate of fossil-fuel CO₂ in geologic time, *J. Geophysical Res. Oceans*, doi:10.1029/2004JC002625, 2005.

Tables

1. Natural and anthropogenic sources of methane, Gton C per year.

Natural Sources

Wetlands	0.075 – 0.15
Termites	0.015

Human Sources

Energy	0.075
Landfills	0.03
Ruminant Animals	0.075
Rice Agriculture	0.05
Biomass Burning	0.03

Figure Captions

1. History of CO₂ and CH₄ concentrations in the atmosphere, from ice cores (symbols) and atmospheric measurements (solid lines). Replotted from IPCC (2001).
2. The impact of various human-related climate drivers on the energy budget of the earth, in Watts per square meter, relative to the year 1750. Replotted from IPCC (2001).

3. Long-term fate of fossil fuel CO₂ , reprinted from Archer JGR.

Projects

1. Long-Term Fate of Fossil Fuel CO₂. Use the on-line geologic carbon cycle model at <http://forecast.uchicago.edu/Projects/geocarb.html>. Use the default setup of the model, and notice that the CO₂ weathering rates etc. for the transient state are the same as for the spinup state. So if there were no CO₂ spike at all, there would be no change in anything at year 0. (Go ahead, make sure I'm not lying about this.) Release some CO₂ in a transition spike, 1000 Gton or more or less, and see how long it takes for the CO₂ to decrease to a plateau. There are two CO₂ plots in the output, one covering 100 thousand years and one covering 2.5 million years. How long does it take for CO₂ to level out after the spike, according to both plots?

2. Effect of Cutting Carbon Emissions. Look at the on-line ISAM global warming model at <http://forecast.uchicago.edu/~archer/Projects/lab.isam.html>.

a. Run the model for the "Business-as-usual" case (Scenario A), and for the cases of halting fossil-fuel and deforestation carbon fluxes now (call it year 2000) and in the year 2050. (The model interpolates between the time points in the input. Zeroing the values in 2075 and 2100, for example, will result in the 2050 emission occurring in 2050, and then a straight line decrease with time to zero in 2075. Therefore you won't be able to shut off emissions abruptly in the year 2050, but the ramp-down will be close enough.) What is the impact of stopping CO₂ emissions now vs. in the year 2050?

3. Climate Sensitivity of this model. Deduce from the above results or new model runs, what is the climate sensitivity, ΔT_{2x} , assumed in this model?

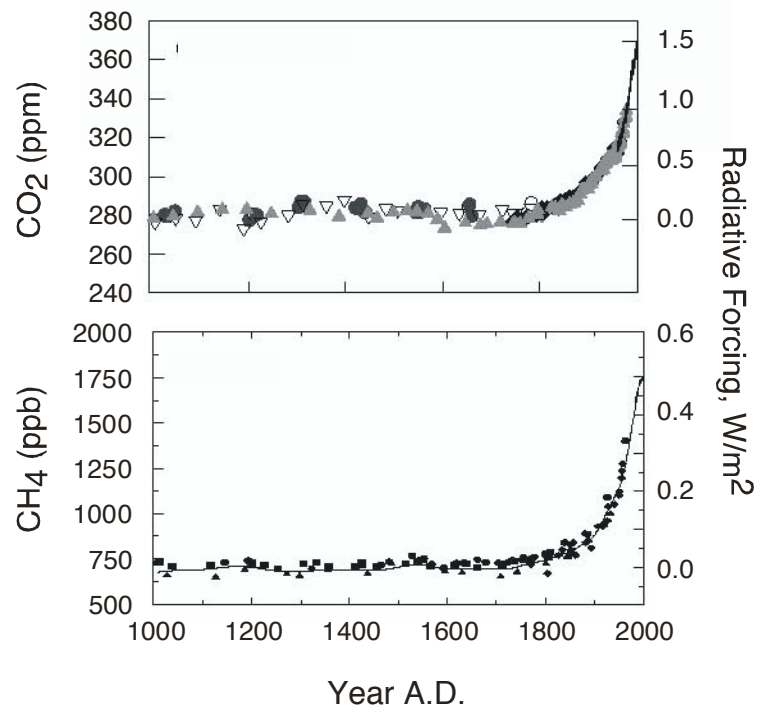


Figure 10-1

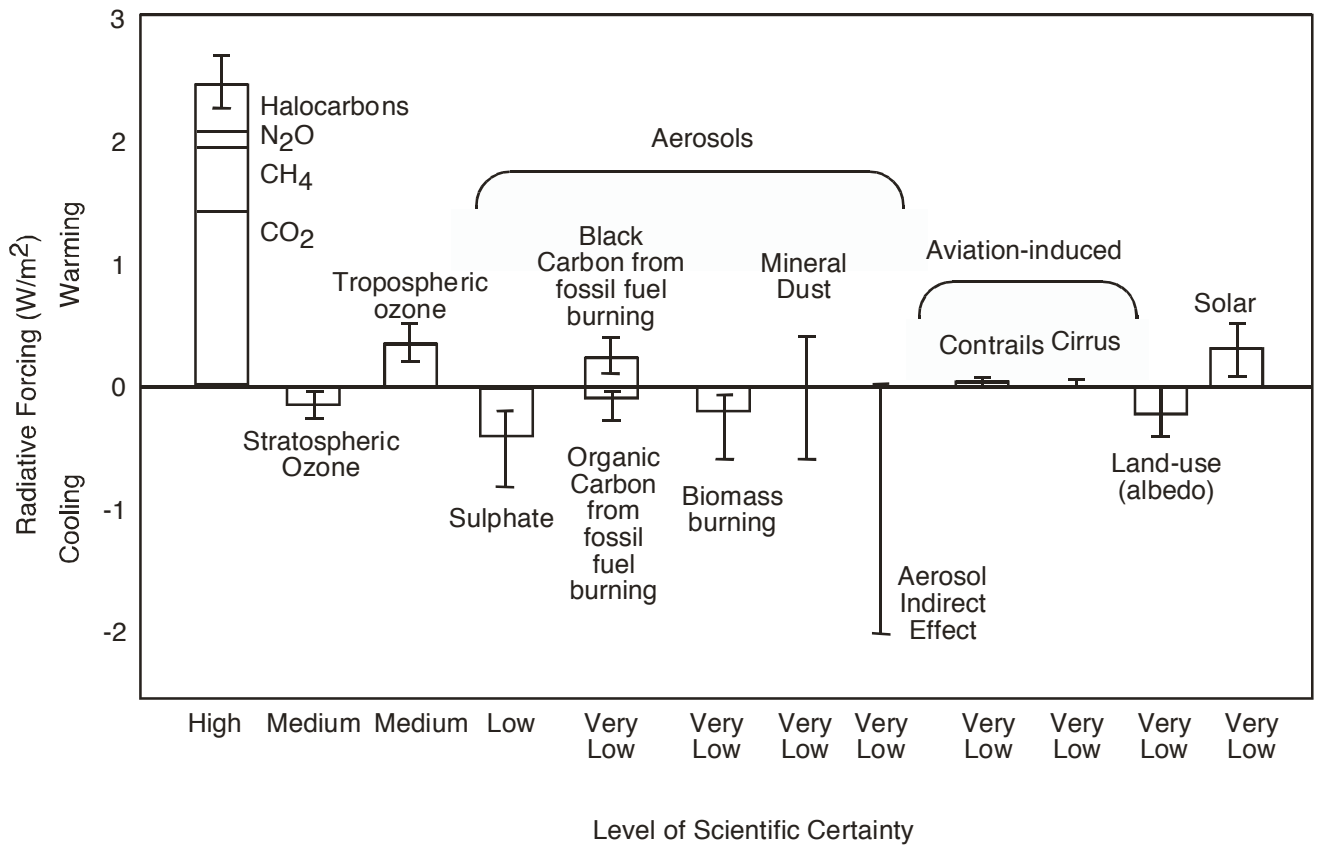


Figure 10-2

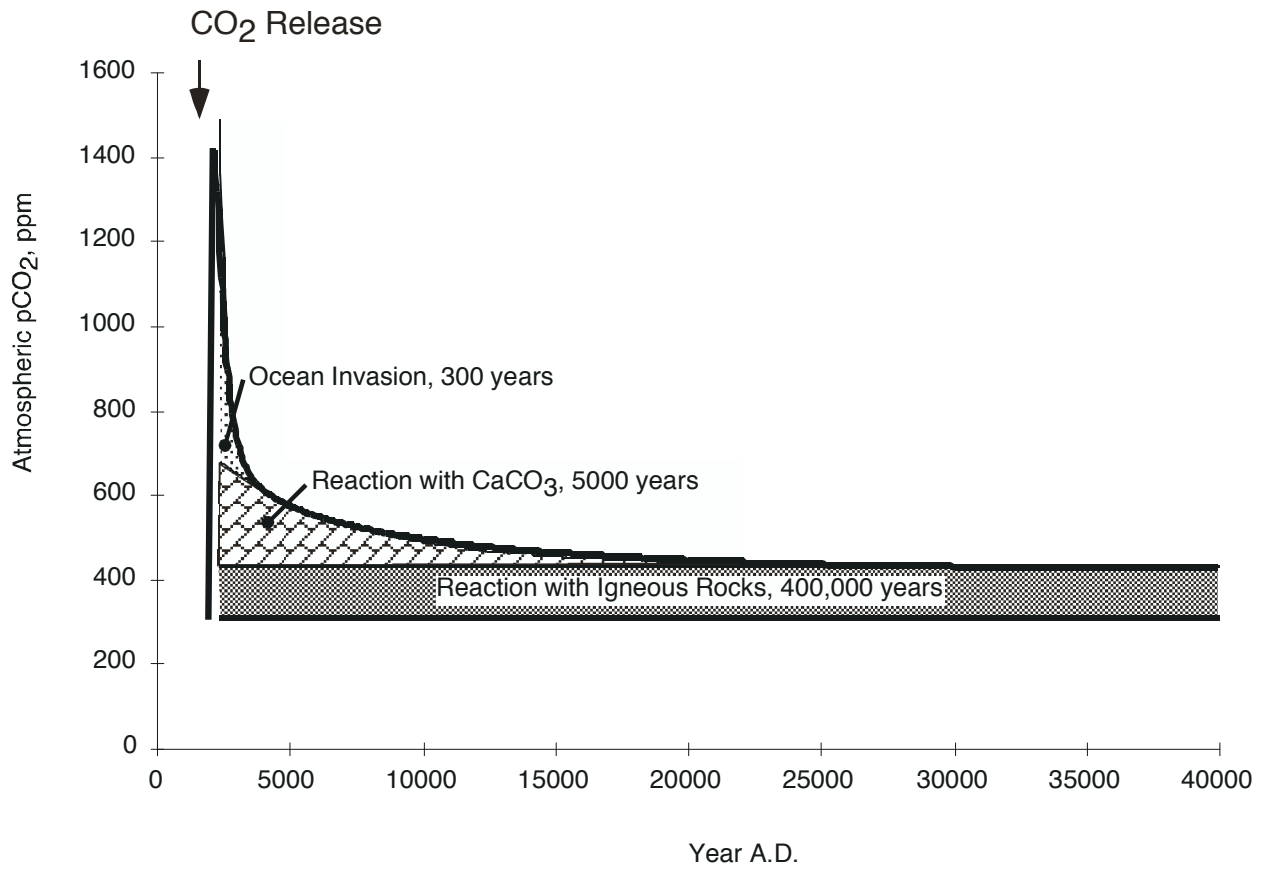


Figure 10-3