Chapter 3

Greenhouse Gases: Some Basics

Scientists know from actual measurements that the amount of solar energy absorbed by Earth is in close balance with the amount of energy radiated back into space as infrared. Furthermore, they know that temperatures measured from satellites at the top of the atmosphere are about 60°F colder than temperatures measured at Earth's surface by the same sensors. This implies that some of the radiation is being trapped in the atmosphere before it is re-radiated back to space.

It is fairly easy to measure how much solar or heat energy the various greenhouse gases absorb, and what parts of the spectrum they do or don't absorb. We know the chemical composition of the atmosphere fairly well, and absorption of infrared by the greenhouse gases is adequate to explain the heat-trapping effect (see Figure 4; also, see Chapter 5).

Given that the reality of the "natural" greenhouse effect is well established, it is logical to conclude that an increase in atmospheric concentrations of greenhouse gases will cause an increase in greenhouse warming. That generality is rarely debated any more by scientists who have specialized in the study of this problem.

What is debated, often passionately, are many other details that make all the difference in environmental policy, and all the difference for the quality of human life over the next few centuries. There has been much recent debate over the amount of greenhouse warming, whether it has begun (or, if not, how soon it will begin), and how long it will take to happen.

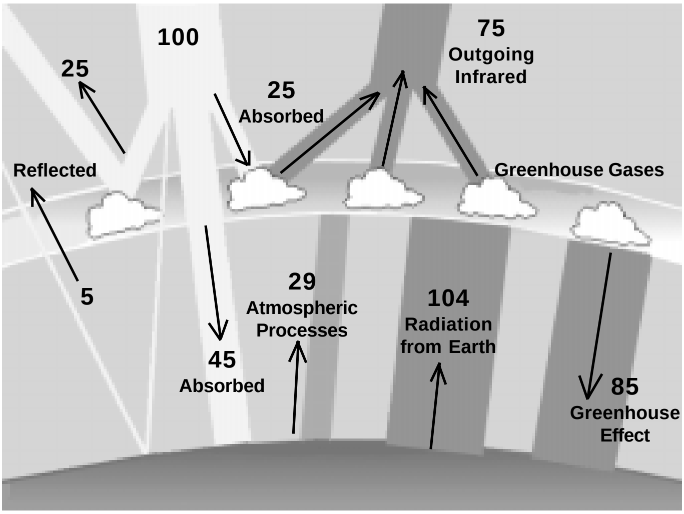
Let's begin with a framework for the greenhouse gases and the roles they play in regulating the climate and in influencing the greenhouse effect, along with an understanding of some areas involving scientific uncertainty.

The Main Atmospheric Gases and Their Roles

Almost all (99 percent, by volume) of Earth's atmosphere consists of two main gases: nitrogen (about 78 percent) and oxygen (21 percent). These gases are important in a number of ways. Oxygen, of course, is vital to the respiration of humans and animals. Both gases play roles in the numerous complex biogeochemical cycles that support life on the planet, but they play almost no direct role in regulating the climate.

The remaining one percent or so of Earth's atmosphere is made of small amounts of a number of "trace" gases. One of the most abundant of these is argon, which for climate purposes can also be ignored. Other

Figure 4. Earth's Radiation Energy Balance



Source: International Institute of Theoretical and Applied Physics, Iowa State University, http://www.iitap.iastate.edu/gcp/forcing/images/greenhouse.gif

trace gases include water vapor, carbon dioxide, nitrous oxide, methane, chlorofluorocarbons (CFCs), and ozone — all of which can be important in the regulation of climate.

Earth's atmosphere is big; indeed, it's staggering. (Its mass is estimated at 5,600,000,000,000,000 tons.) Many people are accustomed to thinking that, because of the enormity of the atmosphere, most human air pollution just dissipates and is eventually so diluted that it becomes harmless. All human clearing and burning of forests for agriculture, and all the smokestacks of industrial civilization, seemingly have not yet changed the basic character of our nitrogen-oxygen atmosphere. As tempting as it is to think this way, it can be a big mistake when it comes to climate change.

For climate, it is the trace gases which are most important. Precisely because their amounts in the atmosphere are so small, pollution and other forces resulting from human activities can alter the proportions of atmospheric trace gases in quite significant ways.

Let's look at the "radiatively active" trace gases — those that absorb or reflect infrared — also known as the "greenhouse gases." Figure 5 summarizes the major greenhouse gases, aside from water vapor.

Water Vapor

Paradoxically, the “gas” which is most important to greenhouse warming is one not normally thought of as a gas at all: water (H_2O). We are used to thinking of water in its common liquid form and seldom as a gas (as vapor or steam). The water vapor in the atmosphere is essentially molecules of steam — evaporated water — bouncing around very thinly diluted among the gaseous nitrogen and oxygen molecules that make up the atmosphere. This water vapor can be experienced as humidity.

Water vapor plays a number of critical roles in affecting both climate and weather. The amount of water vapor in the atmosphere is not at all uniform — far from it — but changes drastically and abruptly, often in a matter of a few hours, to cause, for example, thunderstorms.

It takes a lot of energy to evaporate water. A molecule of water vapor “contains” much more energy than a molecule of liquid water. And quite a bit of water is evaporated every day as the sun shines down on Earth’s vast oceans. In short, water vapor is one of the most important “storehouses” of energy in the atmosphere and in the climate system.

Water loses energy when it condenses into the tiny suspended droplets which make clouds, or into the larger drops which constitute rain. The energy does not disappear, but instead heats the atmosphere. Thus, energy is redistributed through the processes of evaporation and condensation.

When water vapor condenses to form clouds, it has another important effect: it “shades” Earth’s surface and lower atmosphere. In the greenhouse analogy, rolling down a shade over the greenhouse would cool off the interior, just as it would cool a sunny room. (Cloud formation is an important process in the climate system, but one that is hard to quantify and model.) When clouds shade Earth, some of the incoming solar energy is reflected back into space. Some also is absorbed by the clouds and re-radiated upward and downward. Thus, some of the energy is caught at altitudes higher than Earth’s surface, but still in the atmosphere (see Figure 4).

But water in its vaporous state has an important heat-trapping “greenhouse effect.” This is explained by water vapor’s being relatively transparent to the shorter wavelengths at the visible and ultraviolet end of the light spectrum (the form which much incoming solar energy takes). But after this energy has warmed Earth’s surface and been re-radiated upward in the infrared bands of the spectrum, water vapor readily absorbs it — trapping heat in the lower atmosphere (troposphere). Thus, the water vapor is like the heat-trapping “glass” in the greenhouse analogy.

Eventually, this trapped heat finds its way upward and outward and is re-radiated into space. But first it works its way through various parts of the atmosphere. Because incoming solar radiation (now outgoing heat radiation) is thus delayed in returning to space, the temperature of the lower atmosphere is greater than it would be without the water vapor.

Human activities add and subtract water vapor to and from the atmosphere. But these amounts are insignificant compared to the amounts added and subtracted by natural processes. Water vapor is nonetheless important because its atmospheric-warming effects are huge, and because they are hard to quantify, model, and predict. In fact, the amount of water vapor in the atmosphere is determined by the climate at the same time that it strongly affects the climate — a classic “feedback loop.” As discussed later in Chapter 4 under “Role of Clouds,” there is substantial scientific uncertainty about water’s role as vapor or clouds. Since it has both warming and cooling effects, water is a “wild card.”

Figure 5. Major Greenhouse Gases

	Carbon Dioxide	**Methane**	**Nitrous Oxide**	**CFC-11**	**CFC-12**
Pre-industrial Concentration	280 ppmv	700 ppbv	275 ppbv	0	0
Current Concentration	367 ppmv (1998)	1,714 ppbv (1992)	311 ppbv (1997)	262 pptv (1997)	503 pptv (1992)
Growth Rate/yr	0.42%	0.76%	0.24%	-0.76%	1.78%
Human Emissions (million metric tons)	5,455	31	1.3	n/a	n/a
Global Warming Potential (100 yr)	1	21	310	3,800	8,100
Atmospheric Lifetime (yrs)	120	12	120	50	102
Major Sources	Fossil Fuel Combustion, Deforestation	Rice Fields, Cattle, Landfills, Fossil Fuel Production	Nitrogen Fertilizers, Deforestation, Biomass Burning	Aerosol Sprays, Refrigerants, Foams	Aerosol Sprays, Refrigerants, Foams

Drawn from various sources.

Carbon Dioxide

Carbon dioxide (CO_2) is probably the most important of the greenhouse gases released by human activity because its greenhouse impacts are large and because human activities generate so much of it.

Carbon dioxide is a very “natural” ingredient in the atmosphere — so natural that we only quite recently began to think of human-induced carbon dioxide as a “pollutant.” Carbon dioxide can be a good thing, but the key question is: How much of a good thing is too much?

What seems “natural” to humans today can be quite different from what is “natural” from Earth’s larger perspective, because we have been around for only a paper-thin slice (no more than a few million years) of Earth's voluminous 4.6-billion-year geological history.

Some environmentalists fear carbon dioxide buildup will bring about catastrophic changes to the climate (such as those described in *The End of Nature* by Bill McKibben).

For a long time carbon dioxide was probably the dominant active gas in the early Earth's atmosphere. Today CO_2 makes up only about 0.037% of the atmosphere, and the highest estimates are that it could rise to 0.09% by the year 2100 as a result of human activities. Around 4.5 billion years ago, some scientists think it may have made up as much as 80% of Earth's atmosphere, diminishing slowly down to 30% or 20% over the next 2.5 billion years or so. Free oxygen was scarce-to-nonexistent in this early atmosphere, and indeed poisonous to most of the anaerobic life-forms that existed.

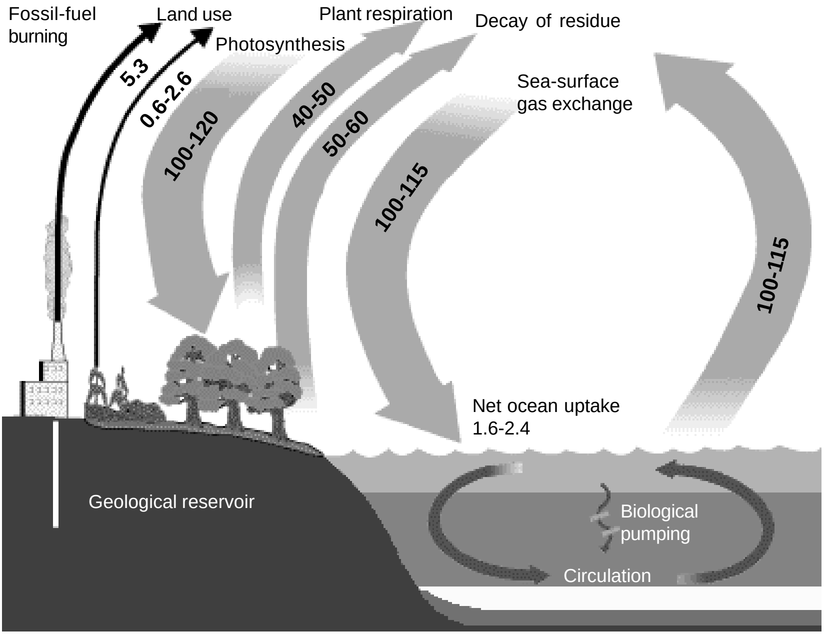
Human life as we know it today would have been impossible in such a CO_2-rich atmosphere. Fortunately for humans and land animals, most of this carbon dioxide was removed from the atmosphere later in Earth's history when sea-dwelling life, the earliest algae, evolved the process of photosynthesis. In photosynthesis, plants use light energy from the sun to turn carbon dioxide and water into sugar and oxygen. Eventually, algae — and more highly evolved organisms, like plankton, plants, and trees — died and locked up most of this carbon in the forms of carbonate minerals, oil shale, coal, and petroleum in Earth's crust. What was left in the atmosphere is the oxygen we breathe today.

Atmospheric carbon dioxide comes from many sources — most of them natural — but is usually brought into balance with "sinks" that drain carbon out of the atmosphere (Figure 6 roughly charts these carbon flows).

One of the biggest "sources" is the exchange of gas between the atmosphere and the ocean surface. This exchange is actually a finely balanced two-way process, but the amounts of carbon dioxide involved are tremendous. When talking about such large amounts of carbon dioxide, scientists translate them into gigatonnes (a billion metric tons) of carbon (GtC) for convenience.

Carbon dioxide can be dissolved in water (the process that makes soda water). It can also be readily undissolved (e.g., soda fizz). The carbon dioxide in the atmosphere is constantly being dissolved in the water on the surface of the oceans, and the sea surface is constantly releasing carbon dioxide back into the atmosphere. These processes are almost entirely physical and chemical. The sea surface releases an estimated 90 GtC/year to the atmosphere, but a number of studies have estimated that this is offset by the 92 GtC/year it takes up. When this activity is netted out, the sea surface exchange is actually a "sink" for

Figure 6. The Global Carbon Cycle



Source: Oak Ridge National Laboratory, http://www.esd.ornl.gov/iab/iab2-2.htm

atmospheric carbon dioxide, taking out more than it puts back.

Most important is the magnitude of these carbon flows relative to other processes, because small changes in the delicate balance (or in our estimates of them) could have a large impact.

Equally important are the biological processes that cycle carbon dioxide to and from the atmosphere. Plants "breathe" in carbon dioxide through the process of photosynthesis — about 102 GtC worth every year. But plants, animals, and other organisms also "breathe" out carbon dioxide. One way they do this is when they "burn" oxygen in the metabolic processes known as respiration. Humans and other land mammals, for example, breathe in oxygen to sustain life and breathe out carbon dioxide as a waste product. Together, all the living things on land are estimated to exhale about 50 GtC/year.

When plants and animals die, the organic carbon compounds they have stored become part of the soil, or forest litter, or swamp muck. Nature composts this "detritus" of life much as gardeners do, by breaking it down through many kinds of chemical decomposition and microbial action. As they break down, soils and detritus are estimated to release about 50

GtC/year back into the atmosphere.

So the 102 GtC taken out of the atmosphere every year by plants is almost perfectly balanced by the total 102 GtC/year put back into the atmosphere by respiration and decay. The magnitude of this cyclic flow of carbon is also important to realize, because small disturbances in the balance can have large implications.

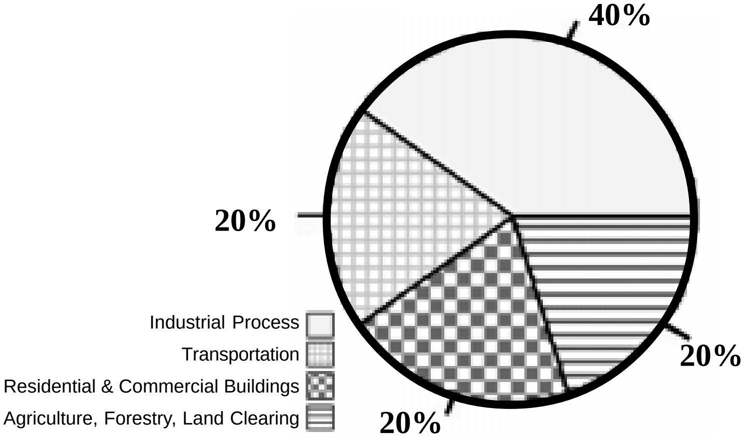
By comparison, the amount of carbon dioxide added directly to the atmosphere as a result of human activities seems at first inconsequential. By burning coal, oil, and natural gas — withdrawing from nature's bank account, as it were — society takes an estimated 5.5 GtC/year out of Earth and puts it into the atmosphere, according to the Intergovernmental Panel on Climate Change. By cutting down and burning forests, humans release perhaps another 2 GtC/year, although there is uncertainty about this amount.

But these amounts do matter, because the natural parts of the carbon cycle (the air-sea exchange and the biological processes) have long been in good balance, at least on the time scales of immediate relevance to humans.

Industrial and agricultural activities seem to have significantly tipped the balance of the carbon cycle.

Many kinds of scientific measurements have shown that the concentration of carbon dioxide in the atmosphere has been increasing over the

Figure 7. Worldwide Generation of CO_2
Total Emissions from Human Activity

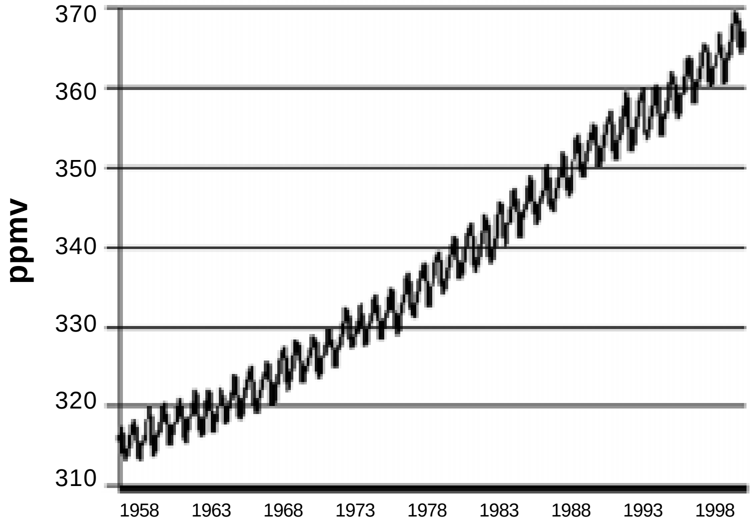


Source: Drawn from Flavin, Christopher; Odil Tunali, June 1996, *Climate of Hope: New Strategies for Stabilizing the World's Atmosphere*, Worldwatch Paper 130 past several centuries. During this time the human population increased geometrically, the steam engine was put to industrial use, the gasoline-powered automobile came into use across the globe, and farmer-settlers cleared native vegetation from vast expanses of the Americas, Australia, and parts of Asia.

During this same period, the atmospheric concentration of carbon dioxide has increased from a pre-industrial (1750) level of about 280 parts per million by volume (ppmv) to about 367 ppmv in 1998, an increase of over 30 percent (see Figure 2, p.12). That's enough to make a potentially significant difference, if climate is as sensitive to greenhouse gases as many scientists think it is. Precise measurements at the Mauna Loa Observatory in Hawaii, far removed from industrial pollution, had charted steady increases from 1958 to 1998 (see Figure 8), with a brief pause in 1990-92.

The close relationship between carbon dioxide concentrations and estimated global mean temperature is striking in Figure 9. Whether the relationship is a causal one, however, is still uncertain. It is tempting to conclude that fluctuations in CO_2 cause temperature changes — but it could be the other way around.

Figure 8. Atmospheric CO_2 Concentrations Derived from In Situ Air Samples Collected at Mauna Loa Observatory, Hawaii



Source: C.D. Keeling, T.P. Whorf, Scripps Institution of Oceanography, University of California, La Jolla, CA

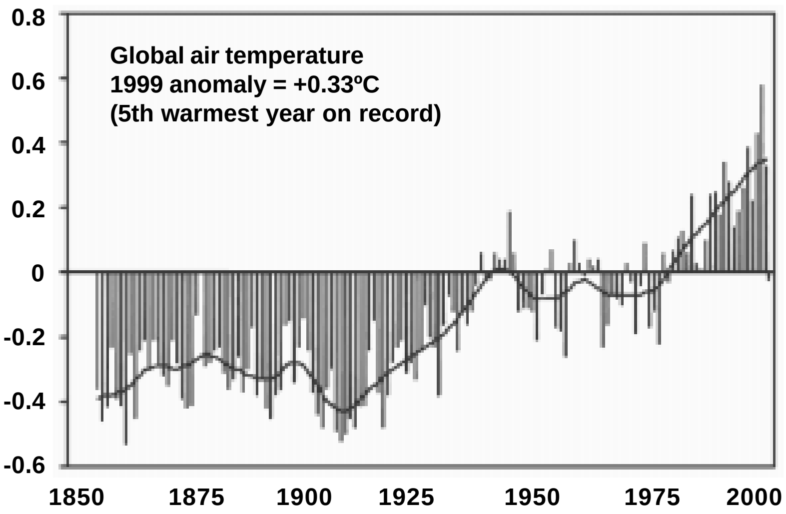
Nitrous Oxide

Nitrous oxide (N_2O) is commonly known as “laughing gas.” Its building blocks are the two dominant gases in the atmosphere: nitrogen and oxygen. Both play important roles in the chemistry of living things (nitrogen goes into amino acids, the “building blocks” of protein and key to metabolism, growth, and repair of tissue). Although nitrogen and oxygen make up some 99 percent of the atmosphere, nitrous oxide is scarce — with a mean concentration of 311 parts per billion by volume (ppbv) in 1992, according to the IPCC (i.e., less than one-thousandth as abundant as carbon dioxide).

The scarcity of nitrous oxide in the atmosphere is countered by its effectiveness as a greenhouse gas: a molecule of nitrous oxide is 200 to 300 times more effective than a molecule of carbon dioxide in the greenhouse warming it produces. Furthermore, it is longer-lived in the atmosphere than carbon dioxide and some other radiatively active gases. Nitrous oxide is eventually broken down by light in the stratosphere into nitrogen and oxygen, but its atmospheric lifetime is about 150 years. As a result, the cumulative effect of any anthropogenic emissions of nitrous oxide will be greater than those of carbon dioxide.

Nitrogen is constantly being taken out of the atmosphere and put into

Figure 9. Global Temperature and Atmospheric Carbon Dioxide



Source: Climatic Research Unit, University of East Anglia, http://www.cru.uea.ac.uk/cru/press/pj9601/index.htm the soil by microorganisms (either alone, or in symbiosis with plants). Nitrogen in the atmosphere (N_2) is fairly inert and largely unusable by living things. The process by which microorganisms convert atmospheric nitrogen into forms such as ammonia (NH_3) which can be used by plants is called nitrogen fixation. After nitrogen is fixed, it may be cycled from the soil into plants and animals many times.

All the while, other microorganisms, in a process called denitrification, are constantly taking nitrogen out of its fixed form in the soil and putting it back into the atmosphere. Besides yielding molecular nitrogen (N_2), denitrification produces nitrous oxide. Scientists estimate that soil denitrification is the dominant source of nitrous oxide going into the atmosphere. Another important contribution comes from natural ocean processes, which are not so well understood.

At the beginning of the industrial age, atmospheric concentrations of nitrous oxide were steady at about 285 ppbv, so the current 311 ppbv concentration represents an 8.8 percent increase. This increase is believed to result from human activities.

Combustion is one source of nitrous oxide, whether burning fossil fuels, wood, or other biomass. But scientists today think combustion may be less important a source of anthropogenic nitrous oxide than the use of fertilizer.

Anyone who has ever struggled with a front lawn knows that nitrogen is the key to making leafy green things grow abundantly. Farmers know this, too. Worldwide, fertilizer production puts some 55 Teragrams (Tg, or 10^{12} grams) of nitrogen into the soil each year. Nitrogen fertilizer is made either by mining nitrates or by “fixing” atmospheric nitrogen (into the usable form of nitrate or ammonium) by industrial processes. When this artificially enriched soil is denitrified, or when fertilizers leach into groundwater, nitrous oxide goes into the atmosphere.

Estimates of the amount of nitrous oxide put into the atmosphere from fertilizer use vary widely — from as low as .01 TgN/year to as high as 2.2 TgN/year. This kind of uncertainty makes it hard to assess the role of nitrous oxide in any human-induced greenhouse warming. The estimated range of N_2O going into the atmosphere annually from all sources is 4.4 to 10.5 TgN/year. That total includes N_2O from oceans, tropical and temperate forest soils, fossil fuel combustion, biomass burning, and fertilizer.

Nonetheless, both combustion and intensive agriculture are part of human culture. Whatever the details of possible human-induced increases in atmospheric concentrations of the greenhouse gas nitrous oxide, they still offer a reminder that human population cannot grow endlessly and still sustain living conditions on Earth.

Methane

Methane (CH_4) is what comes out of the burner on a gas stove, for the most part — natural gas.

As a trace gas in the atmosphere, methane has more warming effect than carbon dioxide — 21 times more on a molecule-for-molecule basis, and 58 times more on a pound-for-pound basis, according to the IPCC.

Another piece of bad news is that concentrations of methane in the atmosphere have increased more than two-fold since the industrial age began — about eight times faster than carbon dioxide. New data suggest the increase may be slowing.

Fortunately, methane's atmospheric lifetime is much shorter than that of most other greenhouse gases — only 8.6 years. Most of it is removed from the atmosphere when it combines with the hydroxyl radical (OH) to form water.

Methane is one of the gases formed in the pressure cooker of Earth's interior, and it is vented through volcanoes and other breaks in Earth's crust. The amount of methane released annually from natural geologic sources has not been measured, forcing scientists to make the assumption that methane sources and sinks closely balance one another in any natural regime, that is, one undisturbed by humans.

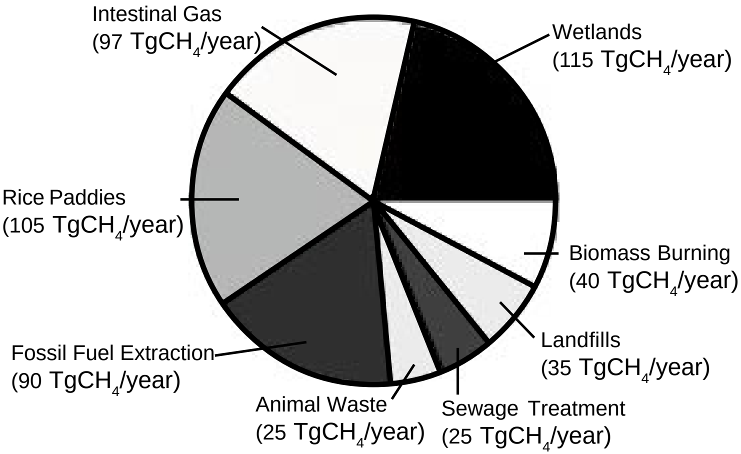
It remains unclear how much methane comes from natural sources and how much from human sources. The totals in the following discussion are only tentative estimates.

Much atmospheric methane is biological in origin. Methane is produced by bacteria in the absence of oxygen (the so-called "anaerobic" bacteria). These bacteria decompose the plant and animal refuse in the black muck of natural wetlands, such as swamps and marshes. Another name for methane is "swamp gas" (its characteristic odor comes mostly from the hydrogen sulfide mixed with it). Wetlands are estimated to produce on the order of 115 $TgCH_4$/year, or about one-fifth of the global total natural and human-induced methane emissions of 570 $TgCH_4$/year.

Another important source of methane is intestinal gas — especially from cattle, water buffalo, sheep, and other ruminant livestock that humans raise in farming. Anaerobic microorganisms in the intestines of these animals make digestion itself possible — but the methane they produce is vented to the atmosphere. This so-called "enteric fermentation" from all animals is estimated to produce about 80-113 $TgCH_4$/year, an appreciable amount, and probably one that varies with the scale of human agriculture. Rice paddies, which in effect are agricultural wetlands specifically created for cultivating rice, are estimated to contribute another 100-110 $TgCH_4$/year.

Other anthropogenic methane sources include fossil fuel extraction

Figure 10. Sources of Methane



Source: IPCC, 1990

(estimated at 80-100 $TgCH_4$/year), animal wastes (25 $TgCH_4$/year), sewage treatment (25 $TgCH_4$/year), landfills (30-40 $TgCH_4$), and biomass burning (40 $TgCH_4$/year). Methane comes from numerous points in our fossil fuel infrastructure — venting from coal mines, venting of gas from oil wells, leaky pipelines, etc.

These estimates have changed significantly in the past few years and remain quite uncertain. Whatever the uncertainties of the estimates, it seems likely that much of the observed increase in atmospheric methane concentrations since the industrial age began has been caused by human activity. It follows that, without technological change, further increases in human population, industry, and agriculture will probably bring further increases in atmospheric methane concentrations.

Halocarbons

Also intensifying the greenhouse effect in Earth's atmosphere are the halocarbons. These compounds combine carbon with one or more of the five elements called halogens: fluorine, chlorine, bromine, iodine, and astatine, but only the first three are relevant here.

Included in the family of halocarbons are the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs), HCFC substitutes, and also some others — carbon tetrachloride, halons, methyl chloride, methylchloroform, and methyl bromide.

Some of these gases, such as CFCs -11, -12, -113, -114, and -115,

Timing for Bringing about Reduced Concentrations

One thing Earth-bound policymakers and journalists need to remember is that greenhouse gas concentrations that have taken decades or centuries to increase will also take decades or centuries to reduce.

It is useful to think of Earth's atmosphere as a large tank, or reservoir, with humans and other sources constantly pumping carbon dioxide into it, and with trees and other "sinks" constantly pumping carbon dioxide out of it. Increased atmospheric concentrations of CO_2 have resulted over a long time from very small changes in the balance between inputs and outputs. Furthermore, scientists believe the climate system may have a significant time-lag before adjusting to more greenhouse forcing.

The problem is that humans can change the inputs and outputs by only small percentages, even if they drastically change their living habits. The consequence of this, in environmental policy, is that an early start on fixing any problem, or at least on preventing it from getting worse, seems to some to be prudent, especially where the "fix" seems to make sense on a number of grounds and where a win-win outcome is possible.

It is sobering to know how long it would take for atmospheric CO_2 to go down, given what science currently knows about the carbon budget, even if humans stopped all of their emissions today. Of course, it is unthinkable that all coal-burning power plants, all gasoline-fueled cars, and all home furnaces would be shut off at once and forever — much less that all chainsaws in the Amazon rainforest would be confiscated. But even if this happened, most models of the carbon cycle suggest that atmospheric CO_2 concentrations would drop only slowly: by a few ppmv every 50 years. The atmosphere would take many centuries to return to pre-industrial CO_2 concentrations.

If humans reduce their emissions by 2 percent a year, atmospheric concentrations will still keep increasing for several decades before they start to even out. On the other hand, if the growth in humans' CO_2 emissions continues at 2 percent a year (a little below the average of recent decades), concentrations could skyrocket as high as 900 ppmv by 2100.

have gotten quite a bit of press. They typically were used in the United States until the mid-1970s as spray-can propellants, solvents, cleaners, and as coolants. Many nations agreed to control emissions of these chemicals in 1987 when they signed the Montreal Protocol on Substances that Deplete the Ozone Layer. That agreement was tightened in 1990, and again in 1992, 1995, and 1997 (see Chapter 5).

The other role which halocarbons play — as greenhouse gases — is often overlooked, but is important to consider.

All of the halocarbons in the atmosphere result from human activities, except for methyl chloride and methyl bromide, which also have important natural sources. The concentration of methyl chloride does not appear to be growing, while the concentration of methyl bromide does. The concentrations of halocarbons in the atmosphere are much lower than those of the other greenhouse gases, typically between .2 and 16.5 parts per trillion by volume.

Halocarbons generally raise some concern because their greenhouse warming effect, on a molecule-for-molecule basis, is drastically greater than that of carbon dioxide. The five ozone-depleting CFCs of most concern have warming effects ranging from 3,000 to 13,000 times greater than carbon dioxide.

Another reason the halocarbons raise concern involves their longevity. Chemical engineers invented some of these chemicals specifically for their stability, a good thing given their purposes. But once in the atmosphere, that very stability becomes a vice: they resist breakdown and removal for many decades. The atmospheric lifetimes of CFC-13 and CFC-115, the longest-lived, are about 400 years, so whatever harmful effects they may have will continue for centuries after we stop putting them into the atmosphere.

Reductions and elimination of CFC production under the international agreement known as the Montreal Protocol has, as a beneficial side effect, help slow the growing concentrations of these greenhouse gases. But some halocarbons with greenhouse potential are not restricted under the Protocol, and some of the CFC substitutes whose uses it will encourage are themselves halocarbons with greenhouse effects.

Tropospheric Ozone — Urban Smog

Ozone has been cast in the roles of both villain and victim in the media during recent decades. Ozone is an everyday part of the atmosphere that plays a number of complex roles and is constantly being created and destroyed.

We are likely to have ozone around as long as we have an atmosphere with abundant oxygen. In its ordinary form as a free element, oxygen usually occurs as a diatomic molecule (consisting of two oxygen atoms) — O_2. Ozone is a triatomic molecule consisting of three oxygen atoms — O_3 — formed when certain kinds of energy, say an electric arc or very intense ultraviolet light, are applied to O_2. Ozone is less stable than diatomic oxygen and most other gases in the atmosphere; every ozone molecule "wants to" give up its extra energy and its extra atom and become oxygen again (see Figure 15, p.59).

Ozone makes the sweetish-pungent smell coming from the arc of electric motors. It is also emitted by laser printers, is created by lightning storms, and is one of the things that makes smog irritate our eyes and lungs.

Most of the ozone in the atmosphere is created when the high-energy ultraviolet rays of the sun reach the rarified gas molecules of the stratosphere. The ultraviolet energy excites the oxygen atoms, and they combine to form O_3.

What is fascinating is that ultraviolet rays both create ozone and destroy it — the high energy ultraviolet rays creating it, and the lower energy ultraviolet rays breaking apart the O_3 molecules. Most ultraviolet rays never reach Earth's surface because O_2 absorbs the high-energy rays, and the low-energy ultraviolet rays are absorbed by ozone. So it is this ozone production and destruction process that absorbs excess ultraviolet and protects humans and other dwellers on Earth's surface from sunburn and skin cancer.

Ozone is not distributed evenly throughout Earth's atmosphere. Most of the naturally occurring ozone tends to be concentrated in the lower stratosphere, where many photochemical reactions involving ultraviolet rays are taking place. These high concentrations are not caused by local ozone production as there is insufficient ultraviolet to produce much ozone at lower altitudes. Ozone concentrations can be strongly influenced by heating and cooling (expansion and compression) and by winds that move it around from place to place.

Some ozone molecules do find their way down into the troposphere. In addition, humans create some ozone in the troposphere by various kinds of air pollution. When automobiles and other human sources emit carbon monoxide, methane, and non-methane hydrocarbons in the presence of nitrogen oxides, sunlight causes a reaction that produces ozone "smog" and raises important public health issues in some of our traffic-choked cities.

Ozone in the upper troposphere and lower stratosphere functions as a greenhouse gas. Just how strong its greenhouse effect is, compared to carbon dioxide, is something scientists have yet to quantify, but it could be much weaker. Measurements of ozone concentrations, especially of historical trends, are few. Some suggest surface ozone may have doubled since pre-industrial times.

Observed Changes and Trends in Greenhouse Gas Concentrations

Along with a strong scientific consensus on the basic physics governing greenhouse effect, as discussed above, scientists generally are quite confident that there has been an increase in the atmospheric concentration of greenhouse gases, and especially of carbon dioxide, over recent decades and centuries. They know this because they can measure it, directly and indirectly.

Precise measurements of atmospheric CO_2 have been taken consistently from instruments at the Mauna Loa Observatory atop a mountain in Hawaii, where the atmosphere is relatively undisturbed by immediate pollution from the urban areas on the continents (see Figure 8 on page 26). The air samples from Mauna Loa are well-mixed, averaging out any local effects of human pollution on the atmosphere at large.

Those measurements show a steady upward trend in the CO_2 concentration since 1958 when measurements began. It increased from about 315 ppmv then to about 367 ppmv in 1998 — about 16.53 percent — according to research published by C.D. Keeling and others.

Scientists can get “historical” air samples by collecting tiny bubbles trapped in the thick ice sheets of Antarctica and other glacial areas. Measurements of these samples show with little doubt that the CO_2 concentration has increased by as much as 25 percent since before the Industrial Revolution, or around 1750.

Are these increases the result of activities undertaken by people? Most scientists studying the matter are convinced that most of the increase results from human actions, although this is a conclusion they arrive at by inference rather than measurement. First, the increase is much larger than the natural variability they observe in CO_2 concentrations over thousands of years. Second, they know how much coal and oil industrial-age societies have burned, and how much forest they have cut down for agriculture, and these factors are enough to account roughly for the increase. Third, isotope analysis of the carbon in atmospheric CO_2 suggests that much of the increase did come from fossil fuel burning.

That said, there may still be some small room for doubt and some need for further understanding. There is no question, for example, that the CFCs are greenhouse gases that result entirely from human activities: Humans developed them, and human actions have led to their release into the atmosphere. Without humans there would be no CFCs. The explanations for increased methane and nitrous oxide concentrations above background levels may be a little more uncertain. Finally, we must remember that the amount of carbon dioxide exchanged with the atmosphere annually by the oceans and land plants is so big that it dwarfs that from human activities. Variations in these processes may account for some of the increase. Scientists are the first to admit they have yet to arrive at any final or precise quantification of Earth's carbon budget.