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Learn About ...

GREENHOUSE GASES
& CLIMATE CHANGE

What is the greenhouse effect?

Life, as we know it, depends on the presence of small amounts of greenhouse gases in the Earth's atmosphere and is affected by changes in the amounts of these gases. The energy flows that keep the Earth livable are represented in Figure 1.

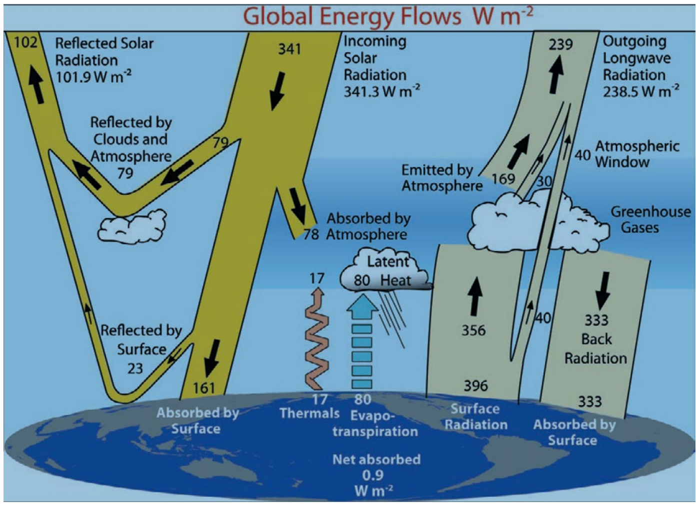

Figure 1. The arrows in this diagram show the amounts of energy entering and leaving the Earth's surface and atmosphere. The values are for the early 21st century and illustrate the net absorption of energy that is increasing planetary warming as human activities are adding more greenhouse gases to the atmosphere.

Source: K. E. Trenberth, J. T. Fasullo. J. Kiehl, 2009, Earth's Global Energy Budget, *Bull. Amer. Meteor. Soc*. **90**, 311-323.

The Earth is warmed by radiation from the sun. Approximately one-third of the sunlight that reaches the Earth is reflected back to space by clouds, small particles in the atmosphere known as aerosols, and light-colored areas – snow, ice and deserts – on the Earth's surface. The rest of the energy, about 240 Watts per square meter (Wm^{-2}), is absorbed by the Earth's surface and atmosphere. Sunlight is primarily visible light, which passes easily through the atmosphere to the ground. To balance this incoming solar radiation, the Earth emits longer wave infrared radiation. Although you can't see infrared radiation, you can feel it on your skin. The warmth you feel from a radiator or from the dark surface of a parking lot, even after the sun has gone down, is infrared radiation absorbed by and warming your skin.

In order to emit 240 Wm^{-2}, the surface of the Earth would have to have a temperature of around −19 °C, which is substantially colder than the present global mean surface temperature of about 14 °C. The reason the Earth's surface is so warm is that some gases in the atmosphere absorb infrared radiation and reradiate some of the warmth back to Earth--as well as to outer space to try to maintain the energy balance. This natural phenomenon is called the greenhouse effect and these greenhouse gases make life, as we know it, possible.

The American Chemical Society's Climate Science Toolkit is available to learn more basic climate science.

What makes a greenhouse gas?

The three most abundant gases in the atmosphere, nitrogen, which makes up 78% of dry air by volume, oxygen, 21%, and argon, about 1%, do not absorb infrared radiation and do not contribute to the greenhouse effect. The two most significant greenhouse gases in dry air, carbon dioxide and methane, are present in the atmosphere at much lower concentrations. Air is not naturally "dry", but always contains some water vapor (humidity) that varies in amount depending on location and temperature. Water vapor is an important greenhouse gas that, on average, accounts for the majority of the greenhouse effect. Sometimes the role of water vapor is forgotten, because, unlike other greenhouse gases, its amount in the air is controlled by local conditions almost independent of any direct human activity.

A molecule can absorb infrared radiation only if there is some way for the radiation and the molecule to interact. When a molecule absorbs infrared radiation, a bond or group of bonds begins to vibrate with greater energy. One type of vibration is the stretching and contracting of a bond between two atoms. Another is bending, the widening and narrowing of a bond angle between three atoms. For a molecule to absorb infrared radiation and be a greenhouse gas, vibrations within the molecule must cause a net change in its dipole moment.

A dipole moment occurs in a molecule when valence electrons are unequally shared in a bond between two atoms and one atom develops a slight positive charge and the other a slight negative charge. For example, in a water (H_2O) molecule, there are centers of positive charge on the hydrogen atoms and a center of negative charge on the oxygen atom. This unequal sharing of electrons or separation of charge results in the molecule having a dipole moment. As the $O-H$ bond stretches, the magnitude of the dipole changes so this vibration will absorb infrared radiation at the same frequency as the oscillating dipole moment. In a nitrogen molecule (N_2) there is equal sharing of electrons and no dipole moment. Stretching the $N \equiv N$ bond does not produce a change in its dipole moment so N_2 does not absorb infrared light.

Some molecules that do not have a permanent dipole moment can vibrate or bend in a way that causes a change in their dipole moment. The most important example for the atmospheric greenhouse effect is the linear molecule, carbon dioxide (CO_2), Figure 2. The molecule does not have a permanent dipole moment, but its electrons are not equally shared between the carbon and oxygen atoms. When the molecule bends or when it undergoes an asymmetric stretch, its dipole moment changes from zero to a nonzero value and these vibrations absorb infrared radiation.

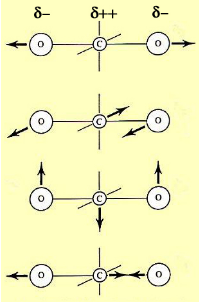

Figure 2. The vibrations of the CO_2 molecule. Charge separation in the molecule is exactly balanced along the linear molecule, so it has no permanent dipole moment. The symmetric stretch (top) does not change the balance; this vibration does not absorb infrared radiation. Bending out of the line (middle two) or asymmetric stretch (bottom) does change the charge balance; these vibrations absorb infrared.

How do greenhouse gases compare to one another?

The strength of the greenhouse warming effect by a greenhouse gas is related to the amount of energy it can absorb from the infrared radiation emitted by the sun-warmed Earth's surface and its lifetime, the length of time it remains in the atmosphere. All molecules containing three or more atoms absorb infrared radiation and, if present in the atmosphere, are greenhouse gases. (Heteronuclear diatomic gases, CO and NO, for example, also absorb infrared radiation, but, if emitted, are so rapidly removed by atmospheric reactions that they are not relevant as greenhouse gases.) Figure 3 is a chart comparing several important greenhouse gases.

			GWP Time Horizon	
Greenhouse Gas	Formula	Lifetime (years)	20 years	100 years
Carbon Dioxide	CO_2	see text	1	1
Methane	CH_4	12.4	84	28
Nitrous Oxide	N_2O	121	264	265
HFC-23	CHF_3	222	10,800	12,400
HFC-134a	CH_2FCF_3	13.4	3710	1300
CFC-12	CCl_2F_2	100	10,800	10,200
Sulfur hexafluoride	SF_6	3200	17,500	23,500

Figure 3. Lifetimes and Global Warming Potentials (GWPs) for several greenhouse gases. The first three have both natural and manmade sources. The last four are only manmade. (HFC = hydrofluorocarbon; CFC = chlorofluorocarbon).

Data source: Intergovernmental Panel on Climate Change (IPCC), fifth assessment report, 2013, Table 8.A.1.

The Global Warming Potential of a greenhouse gas during the time it remains in the atmosphere is calculated as its warming effect compared to the simultaneous addition of the same mass of carbon dioxide to the atmosphere. Carbon dioxide was recognized as a greenhouse gas in the 19th century. At the end of the century, Arrhenius made the first calculation of extra warming due to more atmospheric carbon dioxide from coal burning. Since carbon dioxide is the most abundant greenhouse gas emitted by human activities, it has continued to be the standard against which others are compared.

The fate of extra carbon dioxide emitted to the atmosphere by human activities is complicated. Within a year or so, about half of it has been incorporated into the biosphere or dissolved in the oceans. Over the next two to 20 centuries, the oceans take up about 75% of the remainder and, over 30 to 70 centuries, weathering (mostly reaction with carbonate rock) removes the rest. (See the reference by Archer, *et al*., to find out how these estimates are made.) Thus, about half of all the carbon dioxide humans have added to the atmosphere since the Industrial Revolution is still there and what we continue to add will remain for many centuries, unless a way is developed to remove it.

Methane, CH_4, is the second most important greenhouse gas (in terms of present effect) produced above natural levels as a result of human activities. (See *Learn About: Methane* for background on sources and uses of methane.) Its concentration is only about 1800 parts per billion (ppb)—that is, 1.8 ppm compared to over 400 ppm for carbon dioxide. However, on a molecule-for-molecule basis, methane is about 25 times more effective than carbon dioxide as a greenhouse gas. This is because the more complicated molecule interacts more strongly with infrared light and in wavelength regions where carbon dioxide is transparent. This stronger absorption is partially counterbalanced by methane's relatively short lifetime, about 12-year half-life, in the atmosphere. Methane is oxidized to carbon dioxide and water as it reacts with hydroxyl radicals (present at very low concentrations in the atmosphere).

Human activities that produce nitrous oxide, N_2O, are mostly associated with agriculture and transportation. Given its substantial GWP, it's fortunate that its concentration in the atmosphere is low, a little over about 300 ppb at present.

The man-made compounds in Figure 3 are representative of a large group of fluorine- and chlorine-containing molecules mainly used in refrigerators and air conditioners, as industrial solvents, and as dielectric environments in transformers. They are powerful greenhouse gases, many of which have their effect over long atmospheric lifetimes. The chlorine-containing compounds are also part of the photochemical mechanism that can destroy our vital protective layer of stratospheric ozone. Thus, their manufacture and use are prohibited by international agreement, the 1987 (and subsequent amendments) Montreal Protocol on Substances that Destroy the Ozone Layer. Limiting the production of many of these compounds and developing new ones with shorter lifetimes (HFC-134a, for example) has kept their atmospheric concentrations to a few parts per trillion, so their combined global warming effect is comparable to present levels of methane (but the remaining chlorine- and bromine-containing will continue to exercise their effect on stratospheric ozone depletion until about the middle of the century).

To account for the collective effect of all these greenhouse gases, their individual contributions are expressed in terms of the equivalent amount of carbon dioxide and added to the actual carbon dioxide concentration to give an *effective* carbon dioxide concentration, CO_2e. When reading about climate change or interpreting graphs involving greenhouse gases, be aware whether they are based on CO_2 or CO_2e. Note that water vapor is not included in this summation, even though it is responsible for at least half the greenhouse effect in most locations. This is because it is a *condensable* gas with a concentration that depends on temperature. The other gases are non-condensable and generally well-mixed throughout the atmosphere. Water vapor condenses to liquid and freezes to solid at high altitudes, where the temperature is low and clouds form.

How has the greenhouse effect changed in the past?

During the billions of years that life has existed on Earth, the climate has changed many times, mainly due to changes in the radiation balance. There are three fundamental ways the Earth's radiation balance can change and result in climate change. The amount of incoming solar radiation can change due to a change in the Earth's orbit around the sun or a change in the sun itself. The fraction of solar radiation that is reflected can be altered by changes in cloud cover, land cover, or aerosols. And the proportion of infrared radiation radiated from the Earth's surface to space can be altered by changes in greenhouse gas concentrations.

Figure 4 shows the variations in atmospheric carbon dioxide and temperature over a relatively short period, the most recent 800,000 years. You see that the high peaks in temperature coincide with peaks in carbon dioxide concentration. Increases in greenhouse gas concentration are associated with increases in temperature. The periodic changes (about every 100,000 years) from cold ice ages to warm periods (like the past several thousand years) are caused by changes in the Earth's orbit around the sun and the tilt of its axis. These "wobbles" make small changes in the amount of sunlight that strikes the northern hemisphere and trigger the beginning and ending of the warm periods.

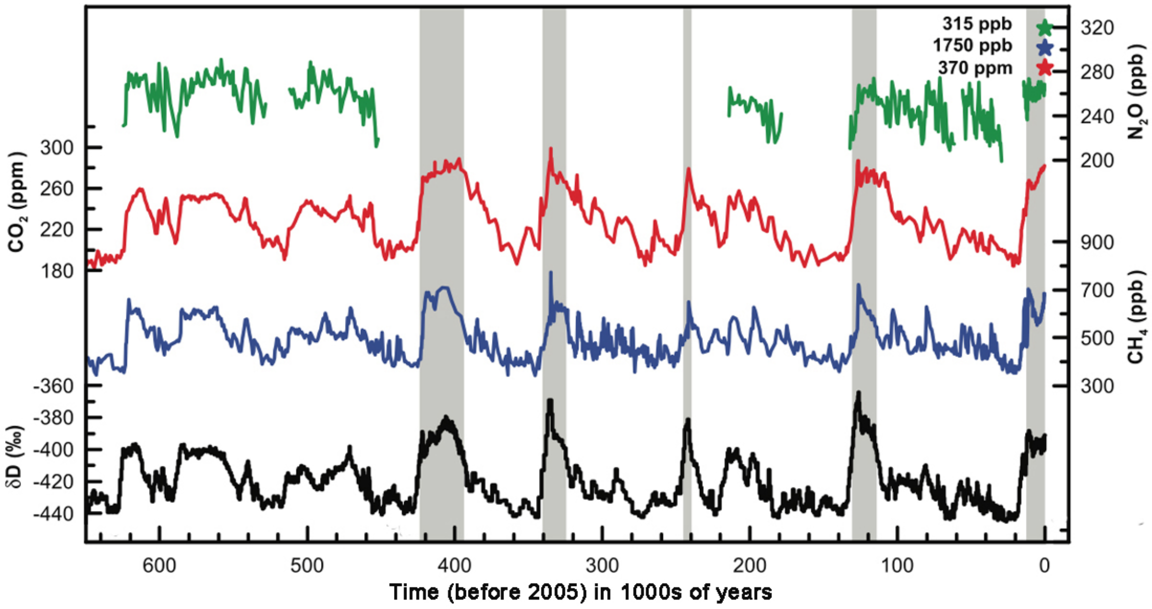

Figure 4. The ice sheet that covers Antarctica has built up over more than a million years. CO_2 (red), CH_4 (blue), and N_2O (green) trapped when the original snow fell is still present in ice cores drilled out of the sheet. Isotopic ratios of the oxygen and hydrogen atoms (black curve) in the surrounding ice are analyzed to give a measure of the temperature when the gas was trapped.

Source: Based on Intergovernmental Panel on Climate Change (IPCC), fourth assessment report, 2007, Figure 6.3.

The temperatures represented in Figure 4 are those on Antarctica, a frigid part of the Earth. The average variation in temperature over the whole Earth during this time span was from about 8-10 °C during the ice-age periods to about 13-14 °C during the warm periods. That is, a 180 parts per million (ppm) CO_2 concentration keeps the planet about 28 °C warmer (-19 °C to 9 °C) than it would be without the greenhouse gas. And a 280 ppm CO_2 concentration keeps it about 33 °C warmer. What would you expect to happen to the temperature as the CO_2 concentration rises to 400 ppm or more?

How is the greenhouse effect changing today?

Currently (as we passed through 400 ppm CO_2 in 2016, Figure 5), the Earth is warming rapidly (on a geological time scale). According to the Intergovernmental Panel on Climate Change (IPCC, fourth assessment report, 2007), "warming of the climate system is unequivocal, as is now evident from observations of increases in global air and ocean temperatures, widespread melting of snow and ice and rising global sea level." In a little over a century, since the late 19th century, the global average air temperature has increased by about 0.84 °C. (For comparison, it took about 100 centuries for the Earth to warm about 4 °C—to its pre-industrial age temperature—after the last ice age.) Between 1961 and 1993, global average sea level rose at an average rate of 1.8 mm/yr. Since 1993, sea level has risen at an even faster rate of 3.1 mm/yr. Satellite data show that Arctic sea ice has shrunk 2.7% per decade since 1978 and that mountain glaciers and snow cover have declined.

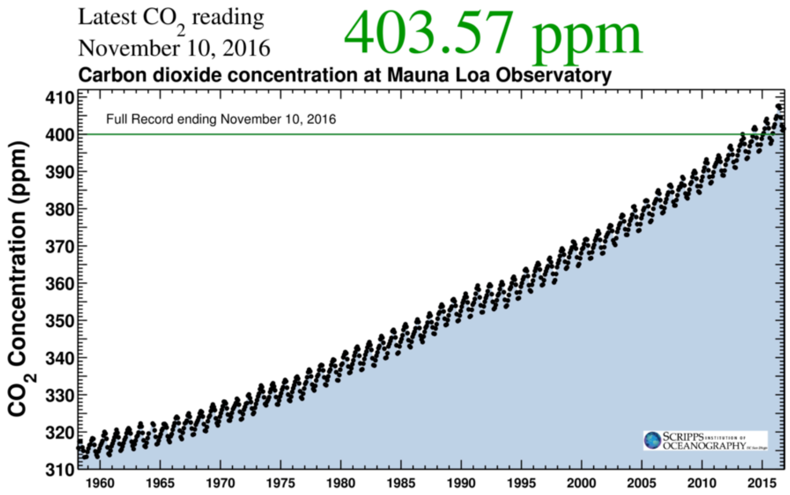

Figure 5. This is the Keeling curve, named for the scientist, Charles Keeling, who began systematic monitoring of the atmospheric CO_2 concentration at a site on the top of the Mauna Loa volcano in Hawaii in 1957. These are the usual measurements quoted in news reports and articles on atmospheric CO_2 levels. Other stations around the world are now also monitoring atmospheric CO_2, but Keeling's are the longest continuous measurements. The daily reading (plus other information) can be obtained at https.//scripps.ucsd.edu/programs/keelingcurve/.

As you might expect, from the data in Figure 4, these observations correlate with increases in CO_2, Figure 6, and other greenhouse gases (GHG) of anthropogenic (human-caused) origin. Global greenhouse gas emissions increased 70% between 1970 and 2004. Figure 6 shows that the atmospheric concentration of CO_2, the most important anthropogenic greenhouse gas, was about 280 parts per million (ppm) before the mid-18th century (with very small human influence) before the Industrial Revolution. The concentration in 2016 has increased to a little more than 400 ppm, Figure 5, and continues to grow at about 2-3 ppm per year, largely due to the combustion of fossil fuels such as coal, natural gas, oil, and gasoline, cement production, and the clearing of forests. The IPCC (fifth assessment report, 2013) concluded that "it is *extremely* *likely* [a greater than 95% probability of occurrence] that human influence has been the dominant cause of observed warming since 1950."

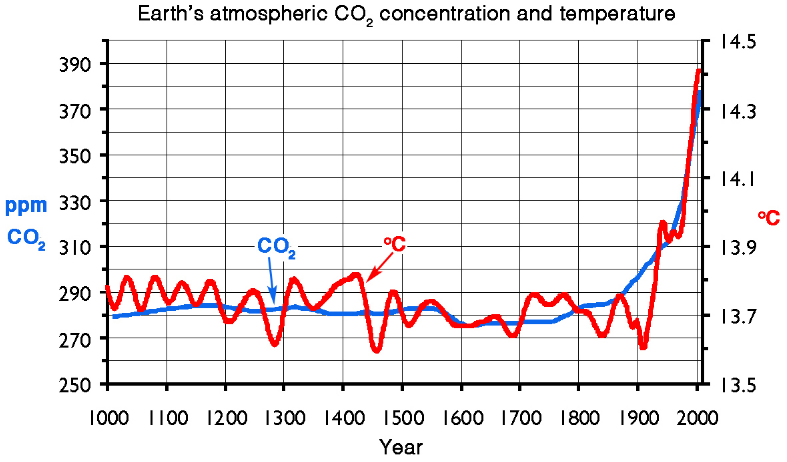

Figure 6. For the first 800 years of the recent millennium, atmospheric CO_2 concentrations and average surface temperatures varied only slightly. After the Industrial Revolution (from about 1750) burning large amounts of coal and then oil and gas have markedly increased the CO_2 concentration and, hence, the temperature.

Source: Wikipedia "co2-temp.png"

The above discussion has focused mainly on carbon dioxide, because it is the most abundant greenhouse gas in dry air and the major gas added as a result of human activities. Natural changes in the concentration of carbon dioxide in the atmosphere are quite slow. (See *Learn About: Carbon Dioxide* for a discussion of the interactions among air, land, and sea that control the natural carbon cycle.) The ice core data above show that increases of 100 ppm or so take thousands of years and decreases take tens of thousands of years. The 120 ppm humans have added in the past two hundred years (and what we continue to add) will be present in the atmosphere for a very long time (unless there is a way, not yet invented, to remove it). This long lifetime is why the greenhouse effects of other gases are usually compared to carbon dioxide.

What about greenhouse gases other than carbon dioxide?

Two substantial sources of atmospheric methane from human activities are the extraction transport, and use of natural gas as a fuel and the large number of domesticated ruminant animals (cattle, sheep, goats, etc.) we use for food and clothing, Natural gas is mainly methane and there is leakage at the wells where it is extracted from the ground, in the thousands of miles of pipelines around the world that carry it to the (leaky) destinations where it is burned for heating and electric power generation. Ruminants have evolved a special, multi-chambered stomach (rumen) that enables them to digest cellulose, the structural glucose polymer that gives plants their stiffness. In their rumen, these animals have bacteria that can break down the cellulose into compounds that can be used as food. Unfortunately, another product of the break down is methane that the animal has to get rid of (or burst). It does this mainly by a good deal of burping (and a very small amount of flatulence). Around the world, research is going on, Figure 7, to find ways to reduce the amount of methane produced by ruminants, both to be kinder to the atmosphere and to turn more of the animal's diet into useful food.

Figure 7. The burps of these Irish cows (containing about 95% of the methane from their rumens) are being monitored to find out if different diets or dietary additives reduce the amount of methane produced as they digest what they eat.

Photo is from the Moorepark Research Centre of Teagasc - The Agriculture and Food Development Authority [of Ireland].

There is also concern that a warming world will speed up natural processes that produce methane. This is an example of a feedback effect where the warming will cause a change that will increase the warming (by adding more greenhouse gas to the atmosphere). Some microorganisms in the decaying organic matter under the water in swamps and bogs produce methane that escapes into the air. (This is the origin of the name "swamp gas" for methane.) In cold northern areas, bogs are generally frozen or very cold for most of the year and these natural processes are slow, so little methane is produced. As global temperature has risen (faster at higher latitudes), these bogs are not as cold and beginning to produce methane at a faster pace.

Other greenhouse gases that have both natural and anthropogenic sources include small amounts of nitrous oxide, N_2O, and tropospheric (lower atmosphere) ozone, O_3 Nitrous oxide is formed by the action of microorganisms on nitrogenous compounds in soil. Human use of large quantities of nitrogenous fertilizers about doubles this natural source. Nitrous oxide is also produced from air at high temperature (when fuels are burned). See *Learn About: Ozone* for discussion of the chemistry of both tropospheric and stratospheric (higher atmosphere) ozone. Natural sources of tropospheric ozone involve the action of sunlight on molecules such as carbon monoxide and methane. The addition of human pollutants, especially from internal combustion engines, adds further photochemical ozone sources. Ozone is reactive and short-lived (a few days), so its concentration and contribution to the greenhouse effect varies from place to place.

A great variety of greenhouse gases that have no natural source are human-manufactured halogen-containing compounds, Figure 3, that have been used mainly as non-flammable, non-toxic refrigerants, The original group of these compounds, the chlorofluorocarbons, CFCs, were used as both refrigerants and propellants in aerosol products. They are so chemically inert, that any that escaped into the atmosphere ultimately made their way into the stratosphere. There, ultraviolet (UV) light from the sun broke them down into species that reacted to begin to destroy the stratospheric ozone layer that protects life on the surface from this deadly UV radiation (*Learn About: Ozone*). The danger was so great that the world's governments came together in the Montreal Protocol to ban the production and use of CFCs. Their concentration in the atmosphere, where they are powerful greenhouse gases (1000s of times more effective than carbon dioxide), is declining and stratospheric ozone has also begun to recover as they disappear.

Replacements for the CFCs, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), which contain a higher proportion of hydrogen atoms and can be destroyed by reactions in the troposphere, were developed. Although only small amounts of these gases that escape reach the stratosphere, they are, unfortunately, also powerful greenhouse gases. Even at their very low concentrations, the combination of halogenated gases in the atmosphere has an effect comparable to that of the methane in the atmosphere. In response to this threat for an even faster increase in the greenhouse effect an international accord was signed in Kigali, Rwanda (October 2016) that binds all nations to phase out the production and use of HFCs—a bit of good news about greenhouse gases.

Another glimmer of hope for global action to mitigate emissions of greenhouse gases is the Paris Agreement, which was negotiated by representatives of 195 countries at the 21st Conference of the Parties of the United Nations Framework Convention of Climate Change (UNFCCC) and adopted by consensus on 12 December 2015. By October 2016, the number of countries that had agreed to meet the goals set for them represented enough of the world's emissions to bring the Agreement into force and it went into effect on 4 November 2016. As of 22 April 2017 (Earth Day) 144 countries, including the two largest emitters, the United States and China, have made their emission reduction commitments.

The Paris Agreement is a hopeful sign that, after more than two decades of meetings, nations seem to have come together to confront the climate disruption caused by human emissions of greenhouse gases. A weakness of the Agreement is that the commitments for reduction in greenhouse gas emissions (decarbonization) are not enough to prevent continued (although slower) build-up of greenhouse gases and hence continuing increase in global temperature. Further, the Agreement has no provision for enforcing the reductions nations have promised and depends on good faith efforts for the common good.

Since the Agreement is not a treaty, United States Senate ratification was not required to take part and the U.S. made its commitment by executive action. Thus, the promised U.S. reductions do not have the force of law and depend upon the policies of each administration, including whether or not to stand by those 2016 promises. The Paris Agreement, although imperfect, was the beginning the world needed to get the emissions-mitigation ball rolling and we can hope all nations live up to their commitments and do all we can to see them enhanced.

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D. Archer, et al., 2009, Atmospheric Lifetime of Fossil Fuel Carbon Dioxide, *Ann. Rev. Earth and Planetary Sci.*, **37**, 1117-134. (From abstract: Equilibration with ocean removes 65-80 % of the CO_2 over 200-2000 years. The rest is removed by weathering over 3000 t0 7000 years.)