

Life  
in

# Greenhouse

**Hot out?  
Blame it on the  
greenhouse  
effect.**

**Y**ou've probably heard about the greenhouse effect and how it has something to do with global warming. And despite your thoughts last January, all of that sounds like bad news.

The greenhouse effect on the planetary scale is actually a good thing—a *very* good thing. Scientists estimate that without some surrounding greenhouse gases, the Earth's average temperature would be a freezing  $-18\text{ }^{\circ}\text{C}$  ( $-0.4\text{ }^{\circ}\text{F}$ ). Tucked inside our security blanket of heat-absorbing gas molecules, we enjoy an average global temperature of  $15\text{ }^{\circ}\text{C}$  ( $59\text{ }^{\circ}\text{F}$ ), and it's rising!

"Greenhouse" is an interesting term for our planetary arrangement. If you've ever wandered through one of those glassed-in greenhouses on a bright sunny day, you were probably happy when the tour was over. Plants appeared to be thriving, but the air temperatures you felt were well above your comfort zone.

The explanation behind a greenhouse effect is actually pretty clear—transparent, in fact. Greenhouse gases allow light to enter, but are far less transparent to the lower-frequency light reflected back toward the atmosphere by objects warmed by the sun.

Light is described as waves of radiant energy with various frequencies and wavelengths. The most abundant molecules in the atmosphere, nitrogen ( $N_2$ ), oxygen ( $O_2$ ), and argon (Ar), compose 99% of the atmosphere and offer only minimal obstacles to the passage of radiant energy. As far as those molecules are concerned, radiant energy can pass through in either direction.

When radiant energy strikes the earth, much of it is absorbed and the surface gets hotter as a result. Warm objects emit radiant energy with a set of wavelengths that are collectively called infrared (IR).

For certain molecules in the atmosphere, the frequency of the radiant energy they encounter makes an enormous difference. For these so-called *greenhouse* gases, some frequencies in the IR region of the spectrum are absorbed temporarily before being re-emitted, often in a direction that sends the IR right back where it came from—the warm surface of the earth.

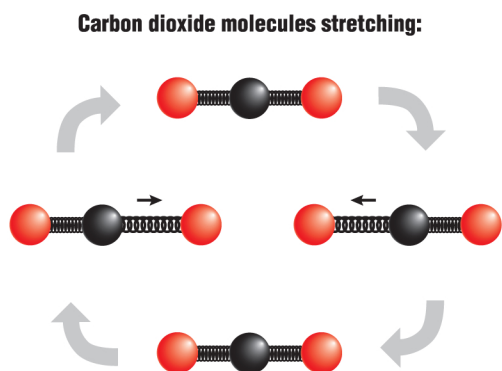
What determines whether an atmospheric gas is an IR energy absorber? You might be able to come up with a hypothesis yourself if you take a close look at the formulas for these non-greenhouse gases— $N_2$ ,  $O_2$ , and Ar; and then a look at the formulas for a few greenhouse gases— $CO_2$ ,  $O_3$ ,  $H_2O$ , and  $CH_4$ . Notice something interesting? Hold that thought!

The fact that molecules are in motion is nothing new to you. That's what explains liquid rising in a thermometer, the smell of fresh bread coming out of the oven, and steam rising from a kettle. But what you might not know is that individual molecules move in another way. They stretch and bend with a kind of vibration unique for each molecule type.

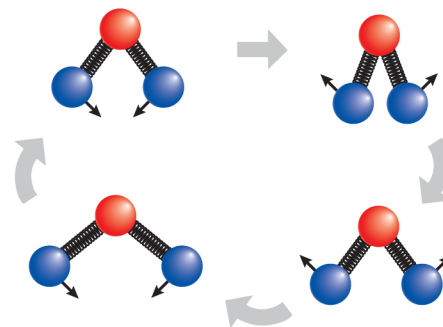
All molecules vibrate, greenhouse and non-greenhouse gas molecules included. Likewise, all molecules are made up of atoms with positive charges centered in the nuclei. When atoms bond together, their collective electrons form a negatively charged cloud surrounding the whole molecule.

When a molecule consists of only two atoms, the only way it can vibrate is for the bond connecting those two atoms to expand and contract. If the two atoms are the same, as in  $N_2$  or  $O_2$ , then this symmetrical stretching motion leaves the positive and negative charges evenly distributed. Isolated atoms, like Ar, cannot vibrate at all.

But for molecules with more than two atoms, there are lots of possible ways that the molecule can stretch, bend, or wiggle. Although some of these vibrations may not distort the charges, there are always some that do. In these, the electron cloud first concentrates more negative charge in one direction before swinging the negative charge in another direction—and then back again.



#### Water molecules bending

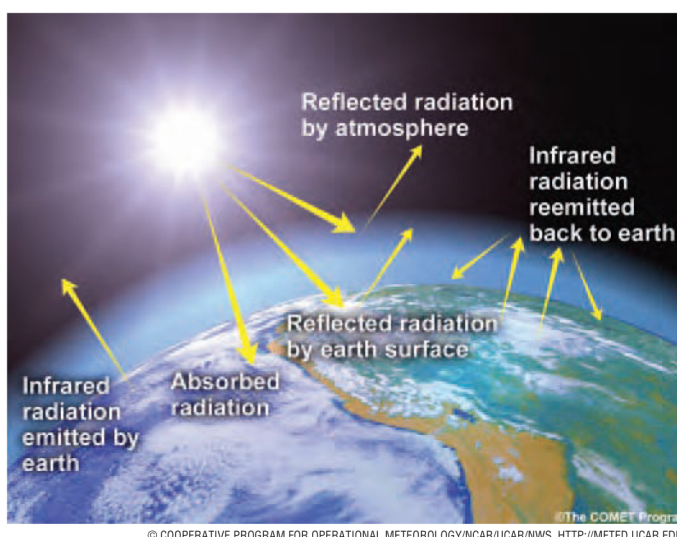


What does this have to do with energy capture? The shifting charges for each of these mixed molecules occurs at a certain frequency. If the frequency happens to match that of radiant energy in the region, the molecule, with its charges already oscillating at that frequency, absorbs that energy in much the same way that someone pushing a swing with just the right frequency adds to the motion of that object.

The earth's warm surface emits the right frequencies of IR for our greenhouse gas molecules. Although they differ slightly in their preferences, these molecules absorb and re-emit IR energy as they stretch and bend.

So, if the gases re-emit the energy, why is there a net warming effect at the earth's surface? Think about a game of ice hockey. The puck skims off in one direction only to be struck with equal force by another player. It may maintain its movement at the same speed, but the direction has changed.

The energy that the greenhouse gas re-emits has a good chance of being directed back down to the earth's surface, or in any other random direction for that matter.



All but about 30% of the solar energy striking our planet gets through the atmosphere to the surface. The other 30% is either reflected back into space by clouds, or in the case of ultraviolet light, absorbed by our fragile layer of atmospheric ozone. Even at the surface, some light is reflected, but much of the energy is absorbed and later radiated as heat.

## Greenhouse gases

Any molecule that vibrates as it absorbs IR is a potential greenhouse gas. But that's where the similarities end and the differences begin. Greenhouse gases vary widely in their effectiveness at absorbing IR. Some excellent absorbers are, fortunately, not very abundant in the atmosphere. But their presence bears some careful watching since a little goes a long way toward retaining heat at the earth's surface.

Greenhouse gas	Relative effectiveness	Abundance in troposphere (%)
Carbon dioxide (CO <sub>2</sub> )	1 (assigned value)	$3.6 \times 10^{-2}$
Methane (CH <sub>4</sub> )	30	$1.7 \times 10^{-3}$
Nitrous oxide (N <sub>2</sub> O)	160	$3 \times 10^{-4}$
Water (H <sub>2</sub> O)	0.1	1
Ozone (O <sub>3</sub> )	2000	$4 \times 10^{-6}$
Trichlorofluoromethane (CCl <sub>3</sub> F)	21,000	$2.8 \times 10^{-8}$
Dichlorodifluoromethane (CCl <sub>2</sub> F <sub>2</sub> )	25,000	$4.8 \times 10^{-8}$

SOURCE: CHEMISTRY IN CONTEXT: APPLYING CHEMISTRY TO SOCIETY, AMERICAN CHEMICAL SOCIETY © 2000

The table above compares both the effectiveness and the relative abundance of some well-known greenhouse gases in the earth's troposphere—the lowest atmospheric layer in which we live and breathe. For the sake of comparison, we'll assign a "1" to the effectiveness of carbon dioxide (CO<sub>2</sub>). Then, we'll assign a "1" to the abundance of water (H<sub>2</sub>O), since it is the greenhouse gas that makes up nearly one percent of the tropospheric mix.

Now, let's take a look at each of these greenhouse gases, realizing as we do so that they act together to form a climate-warming effect as they interact with the earth's systems.

## Water

We mentioned water making up about 1% of the troposphere, but we didn't mention that it is unevenly distributed around our planet—more concentrated over warm bodies of water and equatorial forests, less over the poles and stretches of deserts. Although gaseous water is an effective IR absorber, its total presence in the atmosphere gives us a mixed bag of effects. Water droplets in clouds can actually work in two ways. Depending on the location and the type of cloud, water in lower-altitude clouds is good at reflecting incoming light of all wavelengths back into space, thus shielding the earth. The opposite is true of higher clouds. Their net effect is to trap outgoing IR radiation on its way out of the atmosphere.

## Carbon dioxide

Carbon dioxide may not be the most effective greenhouse gas on the chart, but its collective abundance in the atmosphere results in the capture and retention of nearly half of the outgoing energy in the peak IR wavelength region of the spectrum. Carbon dioxide does not typically react with other molecules in the atmosphere. As a result, it forms a stable gaseous mantle, its concentration tapering off gradually with increased altitude.

Like water, carbon dioxide is intimately involved with all living and formerly living matter on the surface of the planet. In preindustrial eras, atmospheric CO<sub>2</sub> mainly cycled in and out of this biosphere, as plants took in CO<sub>2</sub> to make complex carbon compounds and all living things returned the gas as the organic carbon molecules were consumed. Add forest fires and the occasional volcano eruption to the picture, and you have the historical outlines of the earth's carbon cycle.

Not all carbon dioxide returned directly to the atmosphere. Over many eons of earth's history, deposits of plant and animal remains settled in bogs and other areas where decay organisms failed to thrive. As millions of years passed, these remains formed vast energy-abundant deposits. Today, we're completing that interrupted carbon cycling by burning these deposits of oil, natural gas, and coal as fossil fuels. In doing so, we rapidly reload the atmosphere with enormous quantities of carbon. In fact, current estimates show that industrial countries release one metric ton (1000 kg or 2200 lb.) of carbon per person, per year as a result of fossil fuel consumption. In developing countries, the release rate is about one-tenth as large, but it is growing.

## Searching for the sinks

To learn more about the rates at which the earth releases and *sequesters* (stores) its carbon, scientists are actively measuring the carbon dioxide levels at numerous global sites. Measuring concentrations during various growing seasons and at various temperatures, light intensities, altitudes, and humidities, they are beginning to uncover some interesting riddles.

The earth as a whole is actually sequestering more carbon than expected.

The search for natural carbon *sinks* is on. A carbon sink is a location at which the net effect is in favor of removing more carbon from the atmosphere than is being released. Although tropical rain forests are known to absorb enormous amounts of CO<sub>2</sub> as the abundant plants carry out photosynthesis, they are not proving to be the carbon sinks that scientists once predicted.

Rain forest scientists Deborah and David Clark and their research team recently reported some unexpected findings in the April 25, 2003, online version of the *Proceedings of the National Academies of Science* (PNAS). They shared data showing that when equatorial temperatures surpass a certain mean, tree growth and CO<sub>2</sub> intake actually slow down.

If tropical forests are not the important sinks once thought, where might others be located? Currently, northern forests called *boreal* forests and colder areas of the ocean are under study for their contributions—now thought to be significant.



PHOTO: DISC

Tropical forests are CO<sub>2</sub> absorbers. But are they "sinks"?

Can we make our own sinks? A more radical line of research investigates ways to use technology for sequestering carbon dioxide. For the past 30 years, oil companies have been injecting pressurized CO<sub>2</sub> into wells in order to enhance their pumping capacities. Although much of this CO<sub>2</sub> comes from carbon dioxide-filled pockets that are already underground, the technology might be applied toward devising strategies for draining off some excess carbon from the atmosphere.

The United States Department of Energy is conducting geological surveys for locating rock formations with underlying briny water deposits into which CO<sub>2</sub> might be injected. But extreme care must be taken to find stable sites for this potential use. An abrupt release of CO<sub>2</sub> like the one from volcanic Lake Nyos in the African country of Cameroon in August of 1986 can have deadly consequences. The Lake Nyos disaster released 1 billion cubic meters of carbon dioxide in one blast, silently killing 1724 people and countless cattle and other animal life over a 24-hour period. (See "The Lake Nyos Disaster" in the February 1996 issue of *ChemMatters*.)

## Other greenhouse gases

Carbon dioxide and water are literally facts of life on earth. Their cycling in and out of the atmosphere is only partially under human control. The remaining greenhouse gases appearing in the table may be on the increase, but at least they have this going for them: Because we know how they got there, we can probably do something to control their rate of increase in the troposphere.

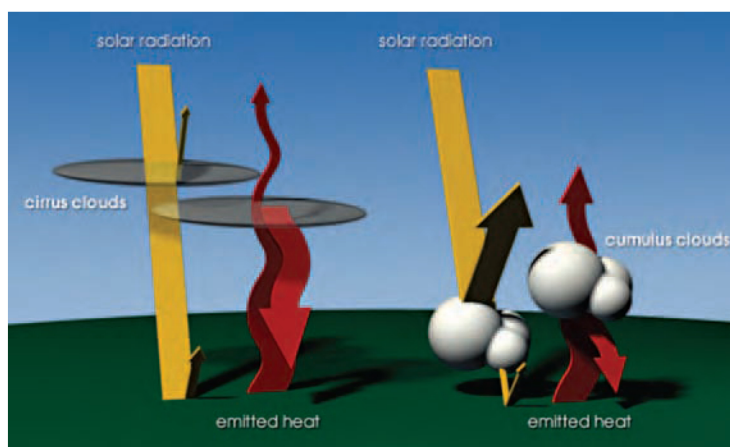
**Methane**, currently present in the atmosphere at 1.7 ppm, has increased to more than twice its level of preindustrial times. A part of the natural "exhaust" from the digestive systems of animals, additional methane is generated by our modern human activities. Petroleum refining releases vast quantities; decaying organic matter in garbage dumps, and large herds of grazing animals are all sources over which we have some control.

**Ozone**, a molecule known for its dual reputation in the atmosphere is also an effective greenhouse gas. Most of the news about ozone is discouraging. In the stratosphere where it is needed for absorbing incoming UV light, it is decreasing. At the same time, it is increasing at ground level as a result of the complex chemical interac-

tions of transportation exhaust chemicals on hot sunny days. Its presence in the resulting photochemical smog is blamed for various health problems and material damages.

As if that isn't bad enough, ozone's effectiveness as a greenhouse gas, particularly noticed in the higher troposphere, is 2000 times greater than CO<sub>2</sub>. Scientists hope that with the widespread use of alternative fuels and better transportation options, tropospheric ozone can be controlled. In fact, many of these measures are already stemming the crisis. Modest attempts to reduce ozone pollution in the United States have resulted in small reductions over the past few decades despite the huge increase in total vehicle miles driven.

The two **chlorofluorocarbons (CFCs)** listed in the table are extremely effective greenhouse gases and are clearly of human origin. Unfortunately, once CFCs are released into the atmosphere, they stay there for a long time. Add that to their IR-absorbing capacities, and you have a dangerous greenhouse gas, even at low concentrations. Today, the net effect of CFCs on global warming is small. Their collective greenhouse gas effect is partially balanced by their infamous



Clouds have different effects depending on their altitudes. Near the surface, they reflect light. High above, they reflect heat back to the surface.

appetite for stratospheric ozone. By reducing ozone's greenhouse effect, they in turn partially cancel their own contribution to global warming. But their ozone destruction comes at a terrible price. Without Earth's thin layer of protective stratospheric ozone, people are at risk for skin cancers and other ailments caused by increased exposure to damaging UV radiation.

Controlling CFCs is already well under way, as the result of the Montreal Protocol, which banned their production in developed countries after 1995. Once valued as effective coolants for refrigeration, CFCs have been replaced by less hazardous alternatives. As a result, they pose much less of a threat to global climate than they did 10 years ago.

As our global population continues to increase, the human contributions to these gases, largely from the burning of fossil fuels, continues to rise. At this time, scientists are resigned to a warming earth over the next century regardless of how we limit our use of fossil fuels. Public policy attention is shifting in the direction of coping with all-but-certain climate changes at the same time that we attempt to slow the rate of warming. ▲

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