Greenhouse Gases Explained

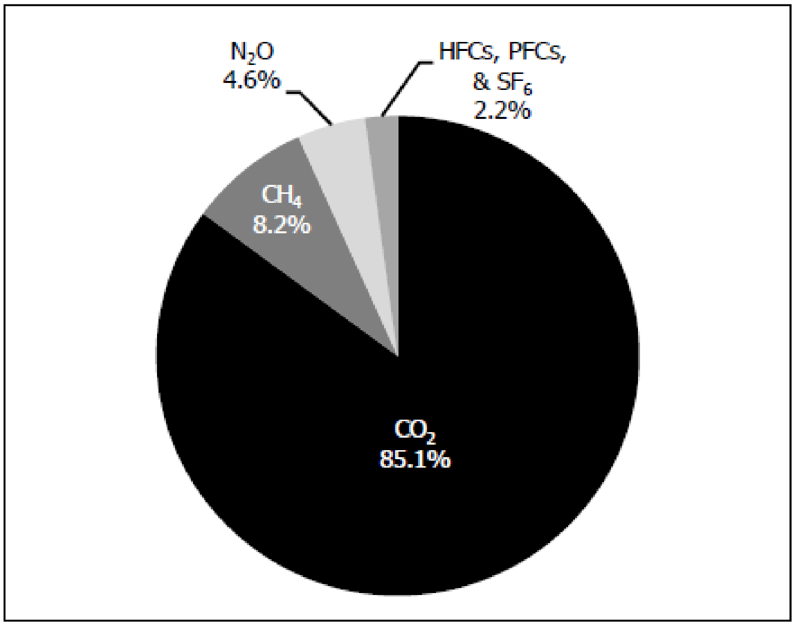
Maggie Y.M. Lee

Up here in New England, not only have we had consecutive months of above-normal temperatures since January, it appears that entire seasons have shifted one month ahead altogether. After the warmest and longest spring on record, tree leaves started to change color near the end of July, the same month that witnessed a series of chart-topping heat waves. By August, some fallen maple leaves are in various shades of pink and red, some pumpkins are turning orange, and acorns are dropping from oak trees onto parched, yellow lawns by the bushel. Are the hints of an early fall simply part of the warmest and driest year in the farmer's almanac? Are the hot and dry summer weather in northeastern U.S., Europe, and Russia, or the devastating floods in southeastern U.S., China, and Pakistan characteristics of El Niño? Or are the above observations more damning evidence of global warming? If you were to ask me about climate change on a bad day, I might say, "We're toast."

It is undeniable that the Earth's temperature is rising due to an increase in the amount of greenhouse gases (GHGs) in the atmosphere. A greenhouse gas (natural or human-made) is one that allows shortwave (solar) radiation to pass through and absorbs longwave (infrared, IR) radiation emitted by the Earth's surface and clouds, in turn emitting infrared radiation from a level where the temperature is colder than the surface. Greenhouse gases also reside in the atmosphere for many (10–50,000) years, with increasing concentration and absorbed heat over time. As a result, the absorbed energy is "trapped," thus warming the Earth's surface.

Industrial Processes Contribute to Greenhouse Effect

Water vapor (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and ozone (O_3) are the primary GHGs in the atmosphere. The Intergovernmental Panel on Climate Change (IPCC) uses the global warming potential (GWP) to measure the propensity of one unit mass of a GHG to heat up the atmosphere, relative to one unit mass of CO_2, integrated over 100 years (GWP_{100}). Global warming potentials are used to calculate the total volume of GHGs emitted (in teragrams or million metric tons of carbon equivalent, Tg CO_2 Eq. or MMTCE) in an industrial process. High-GWP gases account for 2.2% of GHG emissions, with CO_2 being the dominant gas emitted (85.1% of domestic emissions), as shown in the figure below.



2008 Greenhouse gas emissions by gas (percents based on MMTCE)

Source: United States Environmental Protection Agency, 2010

Water vapor is the most abundant (by nature, but not most emitted) GHG that is also a determining factor of weather patterns; natural processes in the soil and oceans generate N_2O; plants capture CO_2 for photosynthesis and their decay release CO_2; CH_4 is released in wetlands; O_3 is continually produced and destroyed in chemical reactions in the atmosphere. The ozone layer that exists in the upper stratosphere shields the Earth's surface against ultraviolet (UV) rays that adversely affect the ecosystem and cause skin cancer and cataracts.

Human activities release carbon monoxide (CO), hydrocarbons, and nitrogen oxide (NO_x), which react chemically to produce O_3. Burning of fossil fuels (transportation, power, heating and cooling, industrial manufacturing) releases both CO_2 and N_2O; fertilizers used in farming release N_2O; agricultural activities, natural gas distribution, and landfills release CH_4. Methane emissions can also produce vapor as the gas breaks down in the stratosphere. While we cannot directly affect the amount of atmospheric water vapor, climate changes due to our behavior can substantially alter the atmosphere, most clearly illustrated by the examples of the increased moisture held by warmer air and rising sea-levels resulting from melting glaciers and polar ice caps.

Human activities contribute to climate change (warming or cooling) by causing changes in the amounts and properties of GHGs, aerosols, and cloudiness. Aerosols are small atmospheric particles of varying size, concentration, and composition, which contain naturally-occurring compounds (e.g., mineral dust, sea salt, volcanic dust, biogenic particles emitted from land and oceans) as well as those emitted from human activities (e.g., sulfur compounds, organic compounds, and soot from fossil fuel and biomass burning; surface mining; industrial processes). The burning of fossil fuels is the largest known contribution to climate change. Although deforestation releases CO_2 and reduces its uptake by plants, warming temperatures encourage plant growth, which increases carbon uptake. However, as seen during 1982–1999 when the temperature rose, the amount of CO_2 in the atmosphere increased, indicating that the effect of more plant growth was not sufficient to offset the effects of deforestation and the burning of trees and fossil fuels.

A new *Science* article reported a drought-related decline in such plant growth from 2000 to 2009 despite climbing temperatures. As drought caused by warming reduces carbon sequestration, more CO_2 remained in the atmosphere, which could lead to further warming and another convoluted chain of environmental changes. The changes could affect global food supply and development of biofuels.[1]

In addition to the above, human activities also contribute to the emission of halocarbons, a group of partially-halogenated organic gases containing fluorine, chlorine, and bromine, which are only produced in small amounts naturally but are used extensively in industrial processes. Many of these gases have much longer atmospheric lifetimes and much stronger radiative forcing properties than CO_2.[2] Chlorofluorocarbons (CFCs) were first developed in the 1920s as a substitute for ammonia (NH_3), a refrigerant. Both CFCs and hydrochlorofluorocarbons (HCFCs) became widely used as a foaming agent, a detergent, and a propellant, but in 1974, these gases were shown to be compromising the ozone layer. The CFC and HCFC molecules are broken down by UV radiation in the stratosphere to release ozone-destroying chlorine atoms (bromine-containing halocarbons also destroy ozone). As the ozone layer is depleted, the amount of harmful UV rays reaching the Earth's surface increases. In 1985, the discovery of an ozone hole over the South Pole spurred industrialized nations into action.

Controlling Greenhouse Gas Emissions

Based on the 1985 Vienna Convention for the Protection of the Ozone Layer, the Montreal Protocol was adopted in 1987 as an international framework to control CFC and HCFC usage. The use of CFCs was completely phased out in 1996 and the use of HCFCs will be substantially phased out by 2020. In their place, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6), which do not contain the ozone-depleting chlorine atoms, are used. It was soon evident that these fluorinated substitutes, as well as the original chlorinated fluorocarbons, are all GHGs that contribute to global warming.

The Kyoto Protocol to the United Nations Framework Convention on Climate Change was adopted in 1997 as a measure to control GHG emission. Greenhouse gases that are subject to reduction include HFCs, PFCs, SF_6, CO_2, N_2O, and CH_4. Countries included in Annex B of the Protocol (most OECD countries and countries with economies in transition) agreed to reduce emissions of these gases by at least 5% below 1990 levels in the commitment period 2008–2012. The Protocol entered into force in February 2005.

As reported by the IPCC, the U.S. Environmental Protection Agency (EPA), and the Pew Center on Global Climate Change, HFCs (also known as fluorinated hydrocarbons) are the most common type of the high-GWP gas. They have GWP_{100} values of 124–14,800 and atmospheric lifetimes in the range of 1.4–270 years. They are widely used as refrigerants (industrial and residential refrigeration and air-conditioning equipment, air conditioning in transportation), insulation foam agents (rigid urethane foam, polystyrene), electrical insulation gases, aerosol propellants, cover gases for melting magnesium, etc. The largest source of HFC emission, and the largest source of GHG in general, is leakage from refrigeration, heat pumps and air conditioning equipment. HFCs escape during the manufacture of some types of foam and gradually leak from the foam throughout its life. HFCs are also emitted when fire extinguishers are discharged.

Many solvents used for electronics and metals cleaning contain HFCs and PFCs. These solvents have low boiling points and convert easily to gases (HFCs are emitted when these solvents evaporate) that remain in the atmosphere for thousands of years. PFCs are strong GHGs with GWP_{100} values of 7,390–17,700 and atmospheric lifetimes of 740–50,000 years. A primary source of PFC emission is aluminum production during which gases such as CF_4 and C_2F_6 are emitted as by-products of the smelting process.

Sulfur hexafluoride is an extremely potent GHG with a GWP_{100} of 22,800 and an atmospheric lifetime of 3,200 years. It acts as an insulator in electric transmission and distribution equipment. Most of the emitted SF_6 is released when such equipment is damaged or opened during repair or disposal. Magnesium production and casting are also sources of SF_6 emissions: SF_6 is used to replace sulfur dioxide (SO_2) as an inhibitor or protective cover gas to prevent the oxidation and potential burning of molten magnesium upon exposure to air.

Government agencies, independent environmental initiatives, and research institutions have established partnerships with the various industries to regulate or voluntarily control GHG emissions. While cost is always a factor that prohibits progress, some industries face more technological challenges than others.

In the electronics (semiconductor, thin-film transistor display, and photovoltaics) industry, manufacturers perform plasma etching and CVD chamber cleaning using PFCs (e.g., CF_4, C_2F_6, C_3F_8), nitrogen trifluoride (NF_3), HFC-23 (CHF_3), and SF_6. There are currently no alternatives to the use of fluorinated gases, although the industry has been working on fluorinated substitutes with lower GWPs (still greenhouse gases), process optimization to more efficiently consume fluorinated GHGs and reduce emissions, and abatement or recycling technology to properly contain emitted GHGs.

Upcoming issues of our newsletter and magazine will discuss GHG mitigation technology and incentives, the pros and cons of various gas substitutes, associated costs, and potential risks.

Maggie Lee can be reached at mlee@gasesmag.com

1. M. Zhao, S.W. Running, “Drought-Induced Reduction in Global Terrestrial Net Primary Production from 2000 Through 2009,” Science 20, Vol. 329. no. 5994, pp. 940–943 (August 2010).
2. “Changes in Atmospheric Constituents and in Radiative Forcing,” IPCC Fourth Assessment Report, Intergovernmental Panel on Climate Change (2007).