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Chapter 17

METHANE, CFCs, AND OTHER GREENHOUSE GASES

Donald R. Blake

Our planet is continuously bathed in solar radiation. Although we who are confined to a fixed location on the globe experience day and night, the earth does not. It is always day in the sense that the sun is shining on half of the globe. Much of the incoming solar radiation, about 30%, is scattered back to space by clouds, atmospheric gases and particles, and objects on the earth. The remaining 70% is, therefore, absorbed mostly at the earth's surface. This absorbed radiation gives up its energy to whatever absorbed it, thereby causing its temperature to increase. Be-

Testimony given in hearings before the Committee on Energy and Natural Resources, U.S. Senate, One-hundredth Congress, first session, on the Greenhouse Effect and Global Climate Change, 9–10 November 1987.

The original publication of this paper provided an illustration that has not been included here. This illustration depicts the monthly means and variances of the trace gases trichlorofluoromethane (CFC-11, or $CFCl_5$), dichlorodifluoromethane (CFC-12, CF_2Cl_2), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), and nitrous oxide (N_2O) as measured at the Barbados station of the Global Atmospheric Gases Experiment.

cause solar radiation is absorbed continuously by the earth, it might be supposed that its temperature should continue to increase. It does not, of course, because the earth also emits radiation, the spectral distribution of which is quite different from that of the incoming solar radiation. The higher the earth's temperature, the more infrared radiation it emits. At a sufficiently high temperature, the total rate of emission of infrared radiation equals the rate of absorption of solar radiation. Radiative equilibrium has been achieved, although it is a dynamic equilibrium: absorption and emission go on continuously at equal rates. The temperature at which this occurs is called the radiative equilibrium temperature of the earth. This is an average temperature, not the temperature at any one location or at any one time. It is merely the temperature that the earth, as a blackbody, must have in order to emit as much radiant energy as the earth absorbs solar energy.

All objects emit radiation continuously, mostly in the infrared region. Some of this radiation is absorbed by the atmosphere, which makes it warmer than it would otherwise be. But the warmer the atmosphere the more it emits to the ground, hence the ground is warmer than it would otherwise be. The extent to which the atmosphere absorbs infrared radiation is, therefore, of great importance in determining the temperature of the earth's surface. If the atmosphere absorbs no infrared radiation, the average surface temperature would be well below freezing, about 255 K (-18°C), and so would the air in contact with it. However, the atmosphere does absorb infrared radiation, and as a consequence surface temperatures are higher than they would otherwise be. This warming of the atmosphere and earth's surface has come to be known as the greenhouse effect.

Not all atmospheric gases absorb infrared radiation to the same degree. Indeed, the most abundant ones by far, nitrogen and oxygen, are the least absorbing. Of far greater importance are water vapor and much less abundant gases such as carbon dioxide (CO_2) and ozone (O_3). The atmospheric concentration of CO_2 is about 350 parts per million by volume (ppmv) and is increasing at a yearly rate of about 1 ppmv. [A plot of the CO_2 concentration versus time is given in Figure 5.1 in Chapter 5.] Fossil fuel combustion is the major source of carbon dioxide. About 60% of the carbon dioxide remains in the atmosphere while the rest is absorbed by the oceans or biosphere. Of major concern is whether the oceans and biosphere can maintain pace with carbon

dioxide production, thus keeping the fraction at 60%. If not, the yearly increase in carbon dioxide will continue to rise.

One's first reaction about greenhouse contributions is that something like CCl_2F_2 (CFC-12), at levels of about 0.00045 ppmv and increasing annually at 0.00002 ppmv, would be trivial. However, as was previously mentioned, the greenhouse effect occurs through the absorption of infrared radiation into specific vibrational frequencies of polyatomic molecules in the atmosphere. Infrared radiation of the wavelengths which can be absorbed by CO_2 vibrations are already exposed to absorption by 350 ppmv of CO_2, and absorption by these vibrations is nearly saturated. Increasing the concentration to 351 ppmv will increase the probability of absorption a little, but it is hard to increase the total absorption very much if it is already 99.9%. On the other hand, the amounts of CFC-12, CFC-11 (CCl_3F), CFC-113 (CCl_2FCClF_2), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), nitrous oxide (N_2O), and methane (CH_4) in the atmosphere are much smaller, and absorption in their vibrational frequencies is very far from saturation. Some of these absorptions happen to fall into infrared "windows" in which absorption by H_2O, CO_2, and O_3 are all very weak or nonexistent, and the individual molecules can be as much as 10,000 times more effective in retaining infrared radiation than is the added CO_2 when the latter concentration is already about 350 ppmv. When you consider the effects from increasing concentrations of these halocarbons, N_2O, CH_4, and tropospheric O_3, etc., the combined absorptions from increments in these gases over the past decade become approximately as important as the increment in CO_2 in contributions to the anticipated overall greenhouse effect.

INCREASING CONCENTRATIONS OF SELECTED TRACE GASES

Trace gas concentrations in the atmosphere reflect, in part, the overall metabolism of the biosphere, and the broad range of human activities such as agriculture, production of industrial chemicals, and combustion of fossil fuels and biomass. There is dramatic evidence that the composition of the atmosphere is now changing, due to increased gaseous emissions associated with human activities.

Detailed measurements of various halocarbons have been conducted since 1978 by a number of research groups throughout the United States. Although the absolute concentrations of individual species may vary by as much as 10% between research groups, there is generally good agreement concerning the overall trends.

Chlorofluorocarbons 12 and 11 are the most widely used CFCs at this time. They are globally used in many and varying applications, some of which are as aerosol propellants, refrigerants, and foaming agents for plastics. Both CFC-12 and CFC-11 are increasing at about 5% per year and are now found in the atmosphere at concentrations of about 450 parts per trillion by volume (pptv) and 250 pptv, respectively.

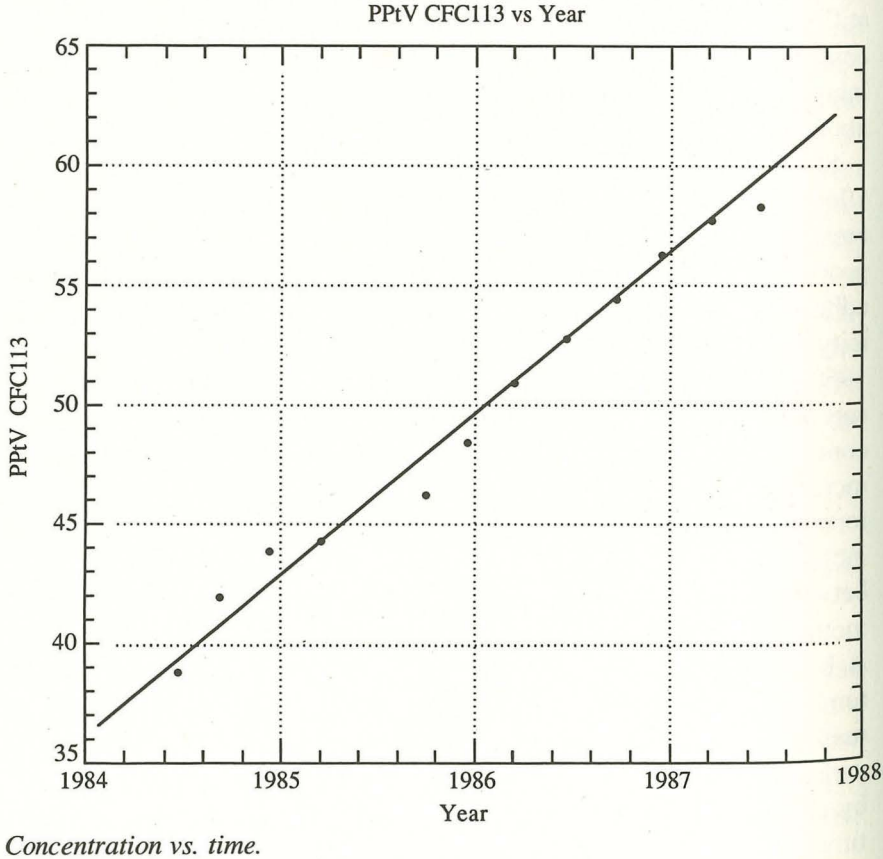
Carbon tetrachloride is used predominantly as a chemical intermediate in the production of CFCs 11 and 12, leading to relatively little emission of carbon tetrachloride to the atmosphere. A small fraction is still used as a solvent in chemical and pharmaceutical production processes. Use as a grain fumigant is declining. The observed rate of increase is about 2%, while the current atmospheric concentration is about 130 pptv.

Stabilized methyl chloroform has been marketed since the early 1960s. Its principal use has always been the industrial degreasing of metallic or metaloplastic pieces. It is widely used for cold cleaning processes in the engineering industry. It is also used as a solvent in adhesives, varnishes, and paints where low flammability and low toxicity are important. Sales of methyl chloroform grew rapidly in the 1960s and early 1970s, when it replaced tri- and perchloroethylene and carbon tetrachloride in many industrial applications. The atmospheric concentration of methyl chloroform in 1987 is about 150 pptv and is increasing at about 7 pptv per year. Global emissions for methyl chloroform are actually higher than that of CFC-12 yet the overall rate of increase is less. This reflects the difference in atmospheric lifetime between these two species, 110 years for CFC-12 and about 7 years for methyl chloroform. The major removal process for methyl chloroform is by hydroxyl radical attack in the troposphere. The only known removal process for CFC-12 is photolysis in the upper stratosphere. The reason methyl chloroform has a relatively short lifetime is due to its carbon–hydrogen bonds. Thus, if the currently used CFCs are replaced by compounds which contain a hydrogen bond, the atmospheric lifetimes will be greatly reduced.

The most recent addition to CFC monitoring among many research groups is that of CFC-113. This compound is used largely as a solvent to clean and deflux sophisticated electronic assemblies and components. Its future use is vulnerable to competing systems, changes in electronics technology, and possible requirements to reclaim the solvent. One can see from the concentration versus time plot given in Figure 17.1 that the large-scale use of this particular species began about the time regulation of CFCs 11 and 12 began in this country. Although this is a difficult species to accurately measure, the atmospheric concentration is about 60 pptv and has a yearly increase of about 7 pptv.

Like the CFCs, nitrous oxide has a long lifetime, about 150 years,

FIGURE 17.1
Atmospheric Concentration of CFC-113: 1984–1987



Concentration vs. time.

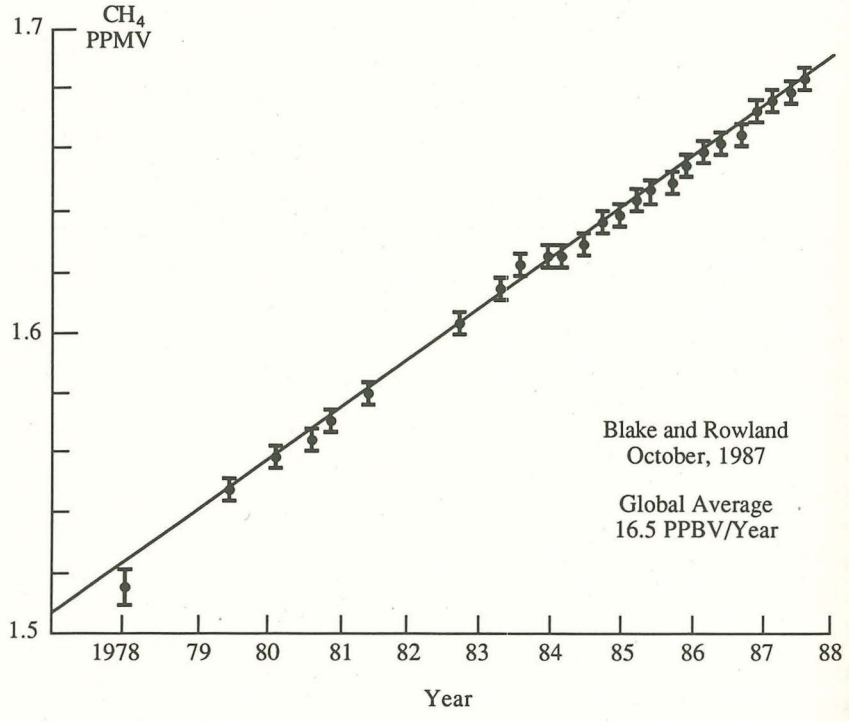
and is destroyed in the stratosphere. There nitrous oxide reacts with oxygen atoms to form nitric oxide, which can catalyze destruction of ozone. However, unlike the halocarbons, whose origins are unquestionably industrial, nitrous oxide has mostly natural sources. Humans may be increasing nitrous oxide emissions from soils by using ammonia and urea fertilizers. The added nitrogen eventually is returned to the atmosphere, partly as nitrous oxide. Burning coal, which contains organic nitrogen compounds, is another anthropogenic source of nitrous oxide. The rate of increase observed for nitrous oxide is about 0.3% or 1 part per billion by volume (ppbv). Currently, atmospheric levels of nitrous oxide are at about 310 ppbv.

The final greenhouse gas to be discussed here is methane. Bacteria produce methane by anaerobic fermentation in wet locations where oxygen is scarce: swamps, peat bogs, other natural wetlands, paddies, and the intestinal tracts of cattle, sheep, and termites. Oil and natural gas exploitation also may be a significant source. Studies of the carbon-14 content of atmospheric methane indicate that at least 80% must have biological origin.

Increases in atmospheric methane could be due to the greater amount of area devoted to rice cultivation or the increased number of cattle. However, increases in atmospheric methane may also be caused by rising levels of carbon monoxide from combustion processes. Both methane and carbon monoxide are removed from the atmosphere largely by reaction with hydroxyl radicals. With both gases competing for a limited amount of hydroxyl, the average lifetime of a methane molecule before it is destroyed may be getting longer. A plot of the methane concentration versus time is given in Figure 17.2. The current world average concentration of atmospheric methane is 1.685 ppmv, while the steady yearly increase observed is about 0.016 ppmv, or about 1%.

The major removal of atmospheric methane occurs in the troposphere; however, about 10% drifts up into the stratosphere. Once there, the methane is oxidized during which water molecules are formed. Two important routes exist for depositing water vapor into the stratosphere. The first is simply being carried upward as water rising in air; the second involves carrying hydrogen atoms upward in the chemical form of methane, and then releasing them as the methane molecule is oxidized. In the 1980s atmosphere, these two processes deliver

FIGURE 17.2
Atmospheric Concentration of Methane: 1978–1987



Concentration vs. time. Growth in tropospheric mixing ratio of methane.

approximately equal amounts of hydrogen to the stratosphere. However, with atmospheric methane concentrations increasing at a rate of about 1% per year, the average amount of water vapor in the stratosphere is presumably steadily increasing with time. An increase in stratospheric water vapor has a binary effect. Water itself is a greenhouse gas and, thus, increasing stratospheric water vapor levels will add to the overall global warming. Secondly, the more water vapor in the stratosphere, the more water there is available to form polar stratospheric clouds, which have been linked to the dramatic losses in ozone over Antarctica during austral spring.

All of the CFCs are not only very efficient at absorbing terrestrial infrared radiation but also play a major role in transporting chlorine atoms into the stratosphere where they can participate in the catalytic destruction of the ozone layer. All of these gases have very long

atmospheric lifetimes, about 110 years for CFCs 12 and 113, 75 years for CFC-11, and about 50 years for the chlorocarbon CCl_4. What this means is that these species drift around until they reach the upper stratosphere. During this lengthy journey, these compounds have been absorbing outgoing radiation being emitted by the earth and redirecting a large portion back towards the ground. Once these gases are high enough in the stratosphere they undergo another absorption, but this time it is with solar ultraviolet radiation, during which a chlorine atom is ejected from the remaining radical. At this point in time we switch from a greenhouse problem to an ozone layer problem. However, because of the extremely long atmospheric lifetimes for these halocarbons, they will have contributed to the greenhouse warming for decades or even centuries before their chlorine begins the catalytic destruction of the ozone layer.

CONCLUSIONS

Carbon dioxide, halocarbons, nitrous oxide, methane, and many more trace gases not mentioned here are all greenhouse gases that can lead to global warming. This warming is not just a theory but reality waiting to happen. These gases also play a major role in determining stratospheric ozone levels. With the unprecedented decrease in ozone above Antarctica in austral spring and recent statistical ozone studies indicating a decrease in Northern Hemisphere ozone levels by as much as 3%, it is not just a theory anymore. The gases that affect these two phenomena are rapidly increasing in atmospheric concentrations due, in part, to the extremely long lifetime of these species. At this point in time, there is no indication from the data being collected that the rate of increase for these gases will decline significantly before the end of the century. The already mentioned long lifetime of some of these gases means that even if all emissions to the atmosphere were completely halted today, many of these species would still be having an effect hundreds of years from now, on global warming and the catalytic destruction of the ozone layer.

THE CHALLENGE OF GLOBAL WARMING

Edited by

DEAN EDWIN ABRAHAMSON

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