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Chapter 15

GLOBAL WARMING, ACID RAIN, AND OZONE DEPLETION

Ralph Cicerone

GASES INVOLVED IN THE GREENHOUSE EFFECT

Scientists now know enough about the properties of chemicals that can be effective greenhouse gases that we can list the potential key contributors to the effect and we can dismiss many other chemicals that do not possess the right properties. In the table of data that accompanies the written text of my testimony (Figure 15.1), I summarize data on greenhouse gases that are actually piling up in the atmosphere. I will read the lines and in between the lines of that table now. You will see that the composition of the atmosphere and hence the greenhouse radiative forcing of the system are entering into uncharted territories.

Carbon dioxide now comprises 346 parts per million (ppm) of Earth's

Testimony given in a joint hearing before the Subcommittees on Environmental Protection and Hazardous Wastes and Toxic Substances of the Committee on Environment and Public Works, U.S. Senate, One-hundredth Congress, first session, 28 January 1987.

FIGURE 15.1
Greenhouse Gases

Gas	Concentration in Air		Present Rate of Increase (per year)
	Pre-Industrial	1986	
Carbon Dioxide (CO ₂)	275 ppm	346 ppm	1.4 ppm (0.4%)
Methane (CH ₄)	0.75 ppm	1.65 ppm	17 ppb (1%)
Fluorocarbon-12 (CCl ₂ F ₂)	Zero	400 ppt	19 ppt (5%)
Fluorocarbon-11 (CCl ₃ F)	Zero	230 ppt	11 ppt (5%)
Nitrous Oxide (N ₂ O)	280 ppb	305 ppb	0.6 ppb (0.2%)
Ozone, Tropospheric (O ₃)	15 ppb?	35 ppb	0.3 ppb? (1%)
Other Fluorocarbons	Zero	see text	Northern Hemisphere Only (5 to 15%)

Key greenhouse gases: present concentrations in air, rates of increase, and preindustrial-era concentrations. Ppm = parts per million, ppb = parts per billion, ppt = parts per trillion.

atmosphere. In the preindustrial era its concentration was about 275 ppm, according to measurements of old air that was taken from ice cores. This 25% increase during the last 100 to 150 years is almost certainly due to our burning of fossil fuels (coal, gas, oil) although part may be due to the decay of organic material following deforestation. Carbon dioxide concentrations are now higher than at any previous time in the last 40,000 years. During that epoch, and possibly for the last 300,000 years, carbon dioxide concentrations have moved between 180 ppm and 300 ppm, never as high as now. There are suspicions that carbon dioxide values were much higher than at present when Earth was considerably younger, several billion years ago, for example.

When carbon dioxide is measured one finds seasonal variations and slightly different values at different locations. Generally, the rate of increase of CO₂ is about 4% per decade; again, this rate varies from year to year. Up to now and for the next 20 years or so, these CO₂ increases account for half or more of the global human-induced greenhouse effect. Future values of atmospheric CO₂ will depend on fuel usage and type, details of exchange with the oceans, and biospheric growth and decay rates. A doubling of preindustrial CO₂ concentrations is not unlikely to occur in 100 to 150 years.

Methane concentrations have risen about 100% in the last 150 years or so, from 0.75 ppm to 1.66 ppm. The last 35 years have seen a 30% to 40% increase. There is no evidence that methane concentrations were

ever as high as they are now although it is possible especially for the primitive Earth. The lower preindustrial concentrations probably represent natural, unperturbed background levels of this familiar gas. Swamps, marshes, and tundra are natural sources of methane ("swamp gas") and natural gas venting is possibly significant. (Methane is the principal component of natural gas.) Human activities are quite capable of having caused these recent methane increases and of continuing such a trend into the future. Humans increase the sources of atmospheric methane by expanding rice agriculture and herds of ruminant animals and by increased coal mining and natural gas drilling and transmission, and possibly by increased usage of landfills as garbage dumps. We may also be suppressing the atmosphere's natural ability to assimilate methane by dumping more pollutants like carbon monoxide into the air. As the climate warms we should be aware of the possibility of accelerated methane releases from tundra and from oceanic methane clathrates.

Methane concentrations are increasing at a rate of 1% per year as shown by direct measurements since 1978. Less direct information indicates that a 35% increase has occurred since 1951, a rate that is consistent with the 1978–86 trend. Further, measurements of old air that was extracted from dated ice cores show that methane concentrations have doubled in the last 150 years or so.

A global warming could liberate methane that is now stored in oceanic sediments or at depth in tundra. This storage involves clathrates, or cages of ice that trap methane and other hydrocarbons. These clathrates are less stable as temperature increases. Scientists have estimated that substantial amounts of methane could be so released, especially from ocean-shelf sediments, but the exact amounts and the timing of the release are not known. One hundred years or more in the future is a good guess.¹

The two principal fluorocarbons that are implicated in the greenhouse effect and stratospheric ozone depletion are fluorocarbon-12 and fluorocarbon-11, CCl_2F_2 and CCl_3F , respectively. These are totally synthetic chemicals so neither of them were present in the preindustrial atmosphere. Fluorocarbon-12 now comprises 400 ppt of the atmosphere and fluorocarbon-11, 230 ppt. These concentrations sound small but both of these chemicals are such potent greenhouse gases and the chlorine atoms that are released from fluorocarbon-12 and -11 in the stratosphere have such large potential for destroying ozone that global

effects are of concern. Also, their concentrations have been growing at rates of roughly 5% per year.

Future increases in atmospheric fluorocarbon concentrations are fully expected. Even if emissions do not increase further, concentrations will increase for the next several decades because of the long time needed for atmospheric destruction processes to equilibrate with a steady input. Emissions to the atmosphere will increase if industrial production and usage increase—there are economic projections that show a continued or growing demand for these chemicals (or possible substitutes) as refrigerants, aerosol propellants, foam-blowing and degreasing agents, and as cleaners or solvents. Without international regulations, the emissions of these chemicals could increase by 2% to 5% annually.

In the case of nitrous oxide (laughing gas, N_2O) we are unsure as to why it is increasing but measurements from all over the world have established that it is. The 1986 concentration of N_2O was about 305 ppb. Preindustrial nitrous oxide concentrations were about 280 ppb. Presently, N_2O concentrations are increasing at about 0.2% per year. This rate might sound small to you but it actually signals a large global perturbation in the source of N_2O . It takes 5,000,000 extra tons of N_2O annually to cause this increase; whatever the identity of this extra source it is now about 25% as big as the total of all natural sources. Two possible N_2O sources seem likely. One is the inadvertent loss of artificial nitrogen fertilizer from fertilized fields and from subsequent nitrogen cycling in food and wastes. Some N_2O escapes into the air from soils and water bodies during two processes of nitrogen cycling: nitrification and denitrification. The second candidate as an N_2O source is the combustion of nitrogen-rich fuels; the higher the nitrogen content of various fuels, the more the N_2O production, it appears. World demand for N fertilizers keeps growing. In 1950 only about 3,000,000 tons were produced. In recent years the annual total was over 50,000,000 tons. Similarly, as you know, fuel combustion increases at 2–4% per year although the mix of fuels varies and the rates track the general economy.

Tropospheric (lower atmospheric) ozone is potentially an important greenhouse gas. Measurements show that tropospheric ozone is increasing in concentration in the Northern Hemisphere (where there is more human influence), perhaps 1% per year, but the situation is not as clear as for other greenhouse gases. Ozone is nowhere near as inert or long-

lived as the others; a blob of ozone-rich air can decay, not just by dilution but also by chemical reactions and contact with surfaces. With only a 100-day lifetime, tropospheric ozone is more variable from place to place and season to season so it's not possible to give one number for a global ozone concentration or rate of change. There are new indications from European scientists that background ozone concentrations at the turn of this century were well below those at present, perhaps only one-third as large. More on ozone later.

Lower atmospheric (tropospheric) ozone is increasing in concentration at the few measurement stations that have gathered good data in the last 10 to 15 years. These data are not as convincing as we would like, but they seem to show a 1% per year increase. Observations from Europe show increases during the 1950s but the proximity of pollution sources confounds the interpretation somewhat. A new, very rigorous, and scholarly reconstruction of data from ozone measurements in France near the turn of this century shows that background ozone levels were well less than today, perhaps only one-third or one-half of today's.

The strongest possibility to explain the ozone increases is that NO_x and hydrocarbon pollutants (that are entering the atmosphere in growing amounts) are reacting through known chemical pathways to produce more ozone. We don't know whether ozone production is greatest near pollution sources like cities or farther downwind in remote areas, nor how effective are NO_x and hydrocarbon emissions from aircraft, but two features of the ozone field data do implicate this general explanation. One is that ozone concentrations have increased more in summer months when photochemical ozone production is easier. Second, the absence of an ozone increase in the Southern Hemisphere, where there is less industry and combustion, is a meaningful sign.²

Other fluorocarbons and chlorocarbons deserve some note. Greenhouse contributions from trichloroethane and carbon tetrachloride are recognized but for other chemicals, for example fluorocarbon-113, whose usages and atmospheric concentrations are growing fast, very little attention has been paid so far, i.e., their atmospheric concentrations and rates of change are poorly known as are some of their infrared properties.

Carbon monoxide (CO) is not an important direct contributor to the greenhouse effect but it has the potential to accelerate the buildup of

other greenhouse gases: methane (CH_4) and ozone (O_3) in the lower atmosphere (troposphere).

CO is an important chemical reactant in the troposphere; through atmospheric chemistry several interesting feedbacks can arise. First, CO reacts with the all-important hydroxyl radical (OH). If adequate amounts of nitrogen oxides (NO and NO_2) are present, O_3 is formed in the sequence of reactions that begins with $\text{CO} + \text{OH}$. Without adequate NO_x , O_3 is consumed in an alternate sequence of reactions. In both cases, atmospheric OH concentrations can be decreased by increasing CO; this occurs when OH and similar radicals combine to form chemicals such as hydrogen peroxide which are susceptible to downward transport and removal, effectively removing OH itself.

In assessing how CO affects methane and ozone, we need greatly improved data on NO_x in the atmosphere. For most of the global atmosphere, though, increasing CO will decrease OH. This would, in turn, cause methane concentrations to increase even if methane sources do not increase.

On balance, available evidence from measurements shows that CO is increasing in the global atmosphere at a rate of 0.5% to 2% per year. CO arises from the incomplete combustion of carbon-based fuels but also from some natural plant emissions; the CO increase could arise from either of these or from any decrease in atmospheric OH concentrations. A final comment—when CO is released into the atmosphere instead of carbon dioxide (CO_2) from some combustion process, one might think that this would favor a slower CO_2 buildup. Actually, CO is converted to CO_2 when CO reacts with atmospheric OH.³

THE GREENHOUSE EFFECT AND STRATOSPHERIC OZONE DEPLETION

An important relationship exists between the causes of the global greenhouse effect and the depletion of stratospheric ozone: the key greenhouse gases fluorocarbons-12 and -11, nitrous oxide, and methane also affect stratospheric ozone strongly. These gases have atmospheric survival times long enough to permit them to make the upward journey into the stratospheric ozone layer. In the harsh ultraviolet light there the fluorocarbons are decomposed yielding chlorine atoms that destroy ozone. Nitrous oxide decomposition yields nitric oxide that acts similarly. Methane acts to slow the attack on ozone but it also decomposes to yield molecular fragments that are involved in ozone destruction.

Interestingly, present models say that the chlorine attack on ozone is slowed somewhat if in the future nitrous oxide and methane continue to increase along with the fluorocarbons. The slower decrease of total ozone will result in a redistribution of ozone toward lower altitudes.

Carbon dioxide is not involved chemically but once in the upper atmosphere it acts to cool the air by radiating energy to space. This cooling should also act to slow the chlorine attack on ozone a little.

Another connection arises because stratospheric ozone itself can affect temperatures at the surface of the Earth. If, for example, the fluorocarbons, nitrous oxide, and methane all increase in the future there should be more ozone present in the lower stratosphere and a warming should occur.

More complicated phenomena may be occurring over the Antarctic where springtime ozone concentrations have decreased greatly in the past fifteen years or so. The same ozone-destroying chemicals just mentioned are probably at play but through more complex pathways, I believe. In any case it is very important to learn the mechanism behind the formation of this Antarctic ozone hole if we want to be able to predict whether the hole will worsen and spread north or whether it will stay over Antarctica or even disappear. Of all the gases relevant today, the fluorocarbons stand out in several ways. Their concentrations in the atmosphere are the smallest, their annual percentage rates of increase are the largest, and their sources are the simplest to understand; they are manmade. Ten years ago CCl_3F and CCl_2F_2 were used mostly as aerosol propellants and as refrigerants and the U.S. accounted for about half the total world production and usage. Now the aerosol application represents a smaller proportion, especially in the U.S., and the U.S. production and usage is a smaller part of the world's. Recently, two U.S. industrial groups proposed that international agreements be sought to limit the future growth of emissions to the atmosphere. In this way steps could be taken to contain future greenhouse and ozone-depletion effects.

ACID DEPOSITION AND GREENHOUSE GASES

The relationships between regional acid deposition and the global greenhouse effect are not as direct as for the greenhouse effect and stratospheric ozone depletion. The strong acids in precipitation, sul-

furic, nitric, and formic, are formed from emissions of sulfur dioxide, nitrogen oxides, and hydrocarbon pollutants. These pollutants are generally short-lived compared to greenhouse gases. None of these pollutants are effective greenhouse gases although nitrous oxide is often formed in the same processes that produce the more common nitrogen oxides. Of the key greenhouse gases only tropospheric ozone is involved in the formation of atmospheric acids.

A strong and broad link between the two phenomena is made, however, through the chemistry of the atmosphere. Hydrocarbon and nitrogen oxide pollutants react to produce ozone. All of these plus carbon monoxide control the rates at which acids are formed by oxidation and they also set the levels of other oxidants, like OH radicals, that bear the atmosphere's ability to oxidize and decompose methane. It is possible that the buildup of methane stems partly from the effects of other pollutants on the whole system. The oxidizing power of the atmosphere is the link and at this time we do not understand very well at all the chemistry of the troposphere where much of this oxidizing power appears.

Note

1-3. Author's response to questions following his testimony.

THE CHALLENGE OF GLOBAL WARMING

Edited by

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