

THIS IS THE TEXT OF AN ESSAY IN THE WEB SITE “*THE DISCOVERY OF GLOBAL WARMING*” BY SPENCER WEART, [HTTP://WWW.AIP.ORG/HISTORY/CLIMATE](http://www.aip.org/history/climate). JUNE 2007. HYPERLINKS WITHIN THAT SITE ARE NOT INCLUDED IN THIS FILE. FOR AN OVERVIEW SEE THE BOOK OF THE SAME TITLE (HARVARD UNIV. PRESS, 2003). COPYRIGHT © 2003-2007 SPENCER WEART & AMERICAN INSTITUTE OF PHYSICS.

Other Greenhouse Gases

While all eyes were turned on carbon dioxide, almost by chance a few researchers discovered that other gases emitted by human activity have a greenhouse effect strong enough to add to global warming. In the mid 1970s, they began to realize that these gases could bring as much damage as carbon dioxide itself. (This essay is supplementary to the core essay on The Carbon Dioxide Greenhouse Effect. For the most important greenhouse gas, water vapor, see the essay on Simple Models of Climate.)

Methane (1859-1970s)

In 1859 John Tyndall, intrigued by the recently discovered ice ages, took to studying how gases may block heat radiation. Since the work of Joseph Fourier in the 1820s, scientists had understood that the atmosphere might hold in the Earth’s heat. The conventional view nevertheless was that gases were entirely transparent. Tyndall tried that out in his laboratory and confirmed it for the main atmospheric gases, oxygen and nitrogen, as well as hydrogen. He was ready to quit when he thought to try another gas that happened to be right at hand in his laboratory: coal-gas. This was a fuel used for lighting (and Bunsen burners), produced industrially by heating coal. It consisted of carbon monoxide (CO) mixed with a bit of the hydrocarbon methane (CH₄) and more complex gases. Tyndall found that for heat rays, the gas was as opaque as a plank of wood. Thus the industrial revolution, intruding into Tyndall’s laboratory in the form of a gas-jet, declared its significance for the planet’s heat balance.

Tyndall immediately went on to study other gases, finding that carbon dioxide gas (CO₂) and water vapor in particular also block heat radiation. Tyndall figured that besides water and CO₂, “an almost inappreciable mixture of any of the stronger hydrocarbon vapors” such as methane would change the climate.¹ But there was far more water vapor circulating, and although CO₂ was only a few parts in ten thousand in the Earth’s atmosphere, that was still much more than other gases. There is so little methane in the atmosphere that it was not detected there until 1948.² In unraveling the causes of the ice ages or any other climate change, there seemed no reason to look further at methane and the like, and for a century nobody paid the matter much attention.

Largely out of simple curiosity about geochemical cycles involving minor carbon and hydrogen compounds, in the 1960s and 1970s, scientists cataloged a variety of sources for methane in the atmosphere. It turned out that emissions from biological sources outranked mineral sources.

¹ Tyndall (1863b); Tyndall (1861); Tyndall (1873a), quote p. 40.

² Migeotte (1948).

Especially important were bacteria, producing the methane (“swamp gas”) that bubbles up in wetlands. That included humanity’s countless rice paddies.¹

These studies, however, gave no reason to think that the gas had any significance for climate change. Thus an authoritative 1971 study of climate almost ignored methane. “To the best of our knowledge,” the review concluded, “most atmospheric CH₄ is produced [and destroyed] by microbiological activity in soil and swamps.” The annual turnover that the experts estimated was so great that any addition from human sources added only a minor fraction. “For this reason, and because CH₄ has no direct effects on the climate or the biosphere, it is considered to be of no importance for this report.” The authors recommended monitoring the atmospheric levels of the gases SO₂, H₂S, NH₃, and even oxygen, but not methane.² There the matter rested through the 1970s.

Ozone and CFCs (1970-1980)

If methane drew little attention, still less went to other trace chemicals in the atmosphere. They were seen as curiosities scarcely worth a scientist’s effort. Up to the 1970s, the atmosphere, as one expert later recalled, “was viewed as inert chemically, and for good reason—most of the chemicals known to be present near the surface were essentially inert.” The air seemed to be just a simple, robust fluid “that transported pollution away from cities, factories, and fires.”³ In the 1950s, a small amount of research did get underway on how various atmospheric chemicals behaved, but only because their interactions were responsible for urban smog. The public had begun to demand action on the smelly and sometimes lethal pollution. Scientists were especially puzzled by the rapidly thickening smog of Los Angeles, so different from familiar coal-smoke hazes. It was a biochemist who finally recognized, by the smog’s peculiar odor, what was going on. When the bright Southern California sunshine irradiated automobile exhaust it created a witch’s brew of interacting compounds, starting with highly reactive ozone.⁴ The scientists who studied ozone chemistry, interested in ground-level pollution, gave no thought to possible connections with global warming.

The history of climate science is full of unexpected linkages, but perhaps none so odd and tenuous as the events that drew public attention to ozone in the upper atmosphere. It began with concerns over a fleet of supersonic transport airplanes that governments envisioned. Beginning in 1970, a few scientists drew attention to the nitrates (NO, NO₂, and in general NO_x) that the jet planes would emit in the stratosphere, along with sulfates (SO₂) and water vapor. They speculated that the chemical aerosols could stimulate the formation of water droplets, altering cloud cover with unknown effects on climate. Moreover, the chemist Paul Crutzen showed that a single nitrate molecule, reacting again and again in catalytic cycles, could destroy many

¹ A pioneer especially for rice paddies was Koyama (1963); wetlands: Ehhalt (1974).

² Wilson and Matthews (1971), p. 242.

³ Cicerone (1999), p. 19, see also H. Schiff’s comments, p. 115.

⁴ Brimblecombe (1995).

molecules of ozone.¹ That could be serious, for the wispy layer of stratospheric ozone is all that blocks harmful ultraviolet rays from reaching the Earth's surface. For the first time, a portion of the atmosphere was shown to be chemically fragile, easily changed by a modest addition of industrial emissions. The ozone problem combined with other, weightier arguments to sink the plans for a supersonic transport fleet.

The new ideas provoked a few scientists to take a look at how the upper atmosphere might be affected by another ambitious project—the hundreds of space shuttle flights that NASA hoped to launch. They found that the chlorine that shuttles would discharge as they shot through the stratosphere might be another menace to the ozone layer. This concern, discussed at a meeting in Kyoto in 1973, helped inspire Mario Molina and Sherwood Rowland to look into other chemical emissions from human activities. The result of their calculations seemed fantastic. The minor industrial gases known as CFCs (chlorofluorocarbons) could become a grave threat to the ozone layer.

Experts had thought that the CFCs were environmentally sound. Industry produced the gases in relatively small quantities. And they were very stable, never reacting with animals and plants—which seemed like a point much in their favor. James Lovelock had decided to track these gases in the atmosphere precisely because they were stable markers of industrial activity. His interest arose from meteorologists' concerns about the haze that was marring summers in rural England—was this actually smog produced by industry? Measuring CFCs, which had no source but human industry, seemed a good way to check this. First Lovelock needed to measure the base-level of the gas, far out at sea. Not without difficulty he managed to do this (his proposal for government funds was rejected and he only semi-officially got a spot on a research vessel). As expected, CFCs were everywhere. Not wishing to stir up environmentalists, in 1973 Lovelock remarked that “The presence of these compounds constitutes no conceivable hazard.”²

In fact, it was exactly the stability of CFCs that made them a hazard. They would linger in the air for centuries. Eventually some drifted up to a high level where, as Molina and Rowland explained, ultraviolet rays would activate them. They would become catalysts in a process that would destroy ozone, threatening an increase of skin cancer and other dangers.³ When scientists

¹ Crutzen (1970) calculated that even small amounts of nitrates could be important as catalysts; this was independently and explicitly linked to supersonic transports and ozone damage by Johnston (1971).

² Lovelock et al. (1973); wryly quoted by Lovelock himself, Lovelock (1974), p. 293; on motives and funding Lovelock (2000), ch. 8.

³ At this point the compounds were called, more precisely, chlorofluoromethanes. Molina and Rowland (1974) (submitted in June); that “the oxides of chlorine... may constitute an important sink for stratospheric ozone” was independently worked out in Stolarski and Cicerone (1974) (submitted in January) but the consequences were not grasped—the first journal to which the paper was submitted rejected it when a reviewer declared the idea was “of no conceivable geophysical consequence”; Cicerone (2003); see also Cicerone et al. (1974) (submitted in

explained that to the public, an agitated controversy broke out over the use of CFCs in aerosol spray cans and the like. The crude but worrisome calculations, and the vehement public response, drove a major expansion of observational and theoretical studies of the stratosphere's chemistry.

If these peculiar gases could do so much to ozone, could they also affect climate? Already in 1973, Lovelock remarked at a scientific conference that CFCs might make a contribution to the greenhouse effect.¹ He followed up by demonstrating that there were unexpectedly high levels of the familiar industrial chemical carbon tetrachloride (CCl₄) in the atmosphere, and warned that it was important to unravel the atmospheric chemistry of all chlorine-bearing carbon compounds.²

Lovelock's findings, combined with Rowland and Molina's warnings that CFCs would linger in the atmosphere for centuries, provoked a closer look into the question by NASA's Veerabhadran Ramanathan (known to his colleagues as "Ram"). In 1975 he reported that CFCs absorb infrared radiation prodigiously—a single molecule could be 10,000 times as effective as a molecule of CO₂. A calculation suggested that CFCs, at the concentrations they would reach by the year 2000 if the current industrial expansion continued, all by themselves might raise global temperature by 1°C (roughly 2°F).³ The following year another group made a more elaborate calculation with a simplified model of the atmosphere, admittedly "primitive" but good enough to get a general idea of the main effects. They reported that if there was a doubling in the atmosphere of two other gases that had previously been little considered, N₂O (nitrous oxide) and methane, these would raise the temperature another 1°C.⁴ Meanwhile Ramanathan's group calculated that ozone too significantly trapped radiation. Keeping its level in the stratosphere high would add to the greenhouse effect.⁵

All these gases had been overlooked because their quantities were minuscule compared with CO₂. But there was already so much CO₂ in the air that the spectral bands where it absorbed radiation were already quite opaque, so you had to add a lot more of the gas to make a serious difference (for more on this "saturation" see the essay on *Basic Radiation Calculations*). A few moments' thought would have told any scientist that it was otherwise for trace gases. Each additional wisp of these would help obscure a "window," a region of the spectrum that otherwise would have let radiation through unhindered. But the simple is not always obvious unless someone points it out. Understanding took a while to spread. Well into the 1980s, the public, government agencies, and even most scientists thought "global warming" was essentially

September); for discussion, Gribbin (1988).

¹ Gribbin (1988).

² Lovelock (1974).

³ Ice-albedo feedback, he added, could give considerably greater warming in arctic regions. Ramanathan (1975).

⁴ Their best guess was 0.7°C for N₂O, 0.3°C for methane, and 0.1°C for ammonia. Wang et al. (1976).

⁵ Ramanathan et al. (1976).

synonymous with “increasing CO₂.” Meanwhile, many thousands of tons of other greenhouse gases were pouring into the atmosphere.

Other Gases as a Major Factor (the 1980s)

In 1980, Ramanathan published a surprising estimate of the contribution to global warming from miscellaneous gases—methane, N₂O, and ozone along with CFCs—produced by industry and also by agricultural sources such as fertilizer. He found that these gases might contribute as much as 40% of the total warming due to CO₂ and all other gases of human origin. He warned that his estimate was highly uncertain and “may become outdated before it appears in print.” Scientists were just beginning to work out the complicated chemical interactions among the trace gases and between each gas and sunlight. For example, it had only recently been recognized how much ozone was generated in the air from other smog chemicals. “The problem,” Ramanathan concluded, “because of its potential importance, should be examined in more detail.”¹

Taking up his own challenge, in 1985 Ramanathan and collaborators looked at some 30 trace gases that absorbed infrared radiation. These additional “greenhouse gases,” the team estimated, added together could bring as much global warming as CO₂ itself.² The announcement shocked the community of climate scientists (for by now the different specialties that dealt with climate followed one another’s work closely enough to form a community). Would the climate changes expected to result from a doubled CO₂ level, a level the world might reach a century ahead, in fact come upon them twice as fast—perhaps within their own lifetimes? The next year Robert Dickinson and Ralph Cicerone addressed the question with a calculation based on the new estimate of the effects of all greenhouse gases. They figured that by the year 2050 global temperature could rise several degrees, “and possibly by more than 5°C,” if self-reinforcing feedbacks took hold. The 22nd century would be even worse.³

Ramanathan and others argued that the potential for global warming gave reason to restrict production of CFCs. However, most of the scientific and public concern was turning to a more immediate problem, the “ozone hole.” This seasonal dearth of protective ozone was discovered over Antarctica in 1985. It seemed likely that CFCs were to blame. Within two years that was demonstrated, as risky flights over Antarctica confirmed new theories of how the chemicals could destroy ozone in very cold air.⁴ The threat of increased skin cancer and other direct harm to

¹ Ramanathan (1980), quote p. 269.

² Ramanathan et al. (1985).

³ Dickinson and Cicerone (1986), quote p. 109.

⁴ Farman et al. (1985); Susan Solomon and, independently, Michael McElroy and Steven Wofsky explained that the unexpected factor destroying ozone was catalysis on the surface of ice crystals in high clouds. For history and scientific references, see Roan (1989); Christie (2000), and reporting by Richard Kerr in *Science* magazine from 1987.

living creatures now seemed imminent, and gave reason enough to further restrict production of CFCs.¹

Appeals from scientists and public activists led to a ground-breaking international agreement, the 1987 Montreal Protocol. It had great success over the following decade in reducing emissions of CFCs. The consequences for climate, however, were ambiguous. Since CFCs exerted a considerable greenhouse effect, the reduction certainly helped restrain global warming. But some of the chemicals that industry substituted for CFCs were themselves greenhouse gases. So was ozone, and as it was restored in the stratosphere, it would add its bit to the warming.

For other emissions such as sulfates and nitrates, scientific and public attention again focused on short-term local harms, the foul smog and acid rain. Some researchers pointed out, however, that these chemicals could affect climate indirectly by forming aerosols that would alter cloud cover. The pollution studies were rapidly building a stock of scientific information about the complex chemistry of the atmosphere, and it seemed increasingly relevant to climate researchers. So did the unsettling news that a gas like ozone, which significantly influenced the planet's radiation balance, could go through large swings. The groups who were constructing complex computer models of climate began worrying how to incorporate atmospheric chemistry as yet another factor in their systems.

After Ramanathan identified methane as a significant greenhouse gas, studies of its role in global carbon cycles accelerated. During the 1980s, scientists came to see that although the methane in the air comes largely from plants and animals, that did not mean human effects were negligible. For humanity was transforming the entire global biosphere. Specialists in obscure fields of research turned up a variety of biological methane sources that were rapidly increasing. The gas was abundantly emitted by bacteria found in the mud of rice paddies and in the guts of cud-chewing cows, among other places. And what about accelerated emissions from the soil bacteria that proliferated following deforestation and the advance of agriculture? Moreover, natural biological activity could be altered by the rise of CO₂ levels and by global warming itself, making for complicated and enigmatic feedbacks.

The importance of all this was driven home by a tentative 1981 report that methane in the atmosphere was increasing at an astounding rate, perhaps 2% a year. The following year, a study of air bubbles trapped in ice drilled from the Greenland icecap confirmed that methane was climbing. The climb, radically different from any change that could be detected in past millennia, had started in the 16th century and accelerated wildly in recent decades.² By 1988, painstaking collection of air samples at many remote locations gave an accurate measure of the recent rise. The actual rate was about 1% a year, bringing a shocking 11% increase of methane in the past decade alone. (Later studies found the rate of rise varying greatly from year to year. During the

¹ Roan (1989), see pp. 92, 195.

² Rasmussen and Khalil (1981a); see Rasmussen and Khalil (1981b); Craig and Chou (1982).

1990s the rise levelled off, for uncertain reasons, but most scientists expected the climb must eventually resume). Each molecule of methane had a greenhouse effect more than twenty times that of a molecule of CO₂. In addition, some of the methane was converted into ozone and water vapor in the stratosphere, where they would exert their own greenhouse effects. It seemed likely that the rising methane level was already having a measurable impact.¹

This raised alarming new possibilities for potentially catastrophic feedbacks. Particularly ominous were the enormous quantities of carbon atoms locked in the strange “clathrates” (methane hydrates) found in the muck of seabeds around the world. Clathrates are ice-like substances with methane imprisoned within their structure, kept solid only by the pressure and cold of the overlying water. A lump of the stuff brought to the surface will fizz and disintegrate, and meanwhile a match can set it aflame. When it became apparent how widespread the clathrates are, they attracted close study as a potentially lucrative source of energy. In the early 1980s, a few scientists pointed out that if a slight warming penetrated the sediments, clathrates might melt and release colossal bursts of methane and CO₂ into the atmosphere. That would bring still more warming.²

The importance of methane became clearer as more cores were drilled from the ice of Greenland and Antarctica, revealing changes in the levels of gases in the atmosphere back through previous glacial periods. Measurements published in 1988 showed that over hundreds of thousands of years, methane had risen and fallen in step with temperature. The level had been a factor of two higher in warm periods than in glacial periods. Perhaps this was due to variations in how much gas was generated by bacteria in wetlands? Or by abrupt releases from undersea clathrates? For whatever reason, there was evidently some kind of feedback between temperature and the level of methane in the atmosphere, a feedback that might gravely accelerate any global warming.³

Ramanathan remarked dryly, “the greenhouse theory of climate change has reached the crucial stage of verification.” If the predictions were valid, he said, the rise in trace gases together with CO₂ would bring a warming unprecedented in human history. He expected it would become apparent before the year 2010.⁴

¹ Blake and Rowland (1988). The levelling off in the 1990s was probably due to the collapse of the Soviet economy, while droughts reduced natural wetland emissions and temporarily held back further rise in the early 2000s, according to Bousquet (2006).

² To be precise, the sediments would release methane, some of which would convert to CO₂. “A potential does exist for significant positive feedback” from Arctic Ocean clathrates, warned Bell (1982), who was stimulated by a 1980 paper presented by Gordon J. MacDonald, see MacDonald (1980).

³ For the last glacial period, Stauffer et al. (1988); Raynaud et al. (1988); for a 160,000 year record Chappellaz et al. (1990); Nisbet (1990).

⁴ Ramanathan (1988), quote p. 293.

After 1988

Attention to gases other than CO₂ continued to grow. Ozone holes in the stratosphere over the poles each winter drove home the idea that even small concentrations of some industrial emissions could have powerful effects. Out of public view, experts delved into the chemical interactions among ozone, nitrates, water vapor, and so forth in every level of the atmosphere from the ground up. Ingenious and difficult computer modeling showed that the concentration of one type of chemical altered the concentration of others, so that the indirect action of a gas could be even greater than its direct greenhouse effect. For example, carbon monoxide (CO) does not intercept much heat radiation by itself, but the massive amounts of the gas that humanity was emitting did alter the levels of methane and ozone. The community of climate scientists could reach no consensus on how serious these complex indirect effects were, and from this point on, the question drove extensive research.¹

Methane got special attention, for it offered some of the most peculiar and unsettling possibilities, such as increased emission from wetlands as the climate warmed. An especially huge reservoir of carbon is locked up in organic compounds in the permanently frozen peat (permafrost), often many meters deep, that underlies Arctic tundras. Around 1990, scientists began to wonder what would happen if a warming climate turned more of the upper layers to marsh. Would biological activity explode in the endless expanses of sodden tundra, with microbes emitting enough methane to accelerate global warming? One of the scientists, Richard Harriss, argued that monitoring methane emissions from tundra could give an early warning of enormous changes.²

Measurements were scanty. But in one especially well-studied Swedish bog, researchers reported an increase in methane emissions from 1970 to 2000 of at least 20 percent, and perhaps much more. By 2006 the thawing of large areas of permafrost was visibly underway in many Arctic regions. There was good reason to expect that much more would thaw by the end of the century. Meanwhile, a 2005 study of the complex chemical interactions in the atmosphere calculated that adding methane was even more powerful in bringing greenhouse warming than previous studies had estimated. It also seemed increasingly likely that clathrates in the warming seabed would release massive amounts of the gas, although (good news for once) that would probably take thousands of years.³ Any of these processes might leave the planet stuck more or less permanently with a climate unlike any that had been seen for many millions of years.

¹ Isaksen and Hov (1987); the greenhouse effect of carbon monoxide was therefore perhaps greater than that of N₂O. Derwent (1990) is cited as a pioneer by Somerville et al. (2007), see pp. 108-9. For a summary, see IPCC (2001), p. 256 and passim.

² Kvenvolden (1988); Harriss et al. (1992); Harriss (1993).

³ Swedish bog: Christensen et al. (2004). Methane: Shindell et al. (2005), Keppler et al. (2006). Clathrates: Archer and Buffett (2005).

Back in 1986, Dickinson and Cicerone had carefully separated the temperature changes that gases might ultimately cause from their immediate and direct physical influence on radiation. They called these direct influences “thermal trappings”—what later came to be called “radiative forcings.”¹ Unlike the ultimate global temperature with its complex feedbacks, the physical forcings could be calculated in a straightforward and reliable way. That made it easier to compare the consequences of changes in the different agents—not only different gases but also aerosols, cloud cover, changes in land vegetation, the Sun's radiation itself, and so on. This subtle but important shift in approach increasingly took hold over the following decade.

In 1990, a report by an international panel of scientists put the idea in a revised form more useful for policy decisions: the “Global Warming Potential.” This included not only the effects of a gas, but also how long it would stay in the atmosphere. That pushed into the very center of policymaking the fact that some long-lingering gases had a potential for warming, molecule for molecule, thousands of times stronger than CO₂.² For example, although the current greenhouse effect from N₂O was not very large, studies found that the gas would remain in the atmosphere for a century or more. And the level was soaring, thanks to emissions from fertilizers and cow manure. Climate scientists had never given this gas as much attention as they gave to methane, with its fascinating biological feedbacks. But by the early 21st century, N₂O had become nearly as important a greenhouse gas as methane. The uncertainties in its production and effects were a serious impediment to rational policy-making.

Experts now agreed that sound policy should take into account all the potential causes of warming. To take one surprising example, leaks of methane from gas pipelines turned out to add significantly to global warming. Meanwhile the headlong rise of methane in the atmosphere seen in the 1970s and 1980s had slowed to a more sedate pace. The reasons were unclear (perhaps the collapse of the Soviet Union's economy, greater efficiencies in production and distribution of the gas, the draining of wetlands?). That drove home the uncertainty of any prediction of future methane levels. Aggressive steps to further cut back inefficient releases of such gases might be the most cost-effective way to begin reducing the risk of harm from global warming. To take another example: restraining the rapid growth in the lower atmosphere of certain aerosol pollutants, like soot from coal-burning, would bring great savings for human health and even agriculture, entirely aside from reducing climate change. Nevertheless, CO₂ continued to hog the spotlight. Other gases (and aerosols) were often overlooked in public arguments, and even in much of the expert policy discussion.

Related: The Carbon Dioxide Greenhouse Effect
Biosphere: How Life Alters Climate

¹ Dickinson and Cicerone (1986).

² IPCC (1990).