Atmospheric Changes Caused by Human Activities: From Science to Regulation

F. Sherwood Rowland
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Human activities are steadily changing the trace gas composition of the Earth's atmosphere. Synthetic chlorofluorocarbon compounds eventually decompose in the stratosphere, releasing ozone-depleting chlorine atoms. The 1987 Montreal Protocol has controlled the further atmospheric release of CFCs, but depleted ozone levels will persist throughout the twenty-first century. Accumulation of carbon dioxide, methane, and other "greenhouse gases" impedes the escape of terrestrial infrared radiation, causing a warming of Earth's surface. The release in urban environments of hydrocarbons and nitrogen oxides, usually from automobiles, creates smog. Emission regulations for greenhouse gases and smog will be major problems in the twenty-first century.

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INTRODUCTION

The state of the environment presents a constant opportunity for cartoonists, and a New Yorker cartoon from about two months ago provides some insight into our present situation. The caption for a confident gentleman read: “I want to preserve the environment just as it is: acid rain, holes in the ozone layer, lots of crap in the air.”1 Observing the responses to our research, I have found that people often respond readily when faced with acute, immediate environmental problems, but, like the man in the cartoon, are reluctant to act toward creeping, long-term adverse environmental developments.

My own scientific research interests lie primarily in understanding the chemistry of the atmosphere: its composition, the changes over time, and the causes for such changes.2 My research group’s studies have produced data that point to three significant atmospheric environmental problems: stratospheric ozone depletion, global warming, and photochemical smog. The changes these problems cause are of great consequence; they are largely caused by human activities and each will play out over a long timescale during the next half century. This Article will briefly explain these environmental atmospheric problems, and will examine the world’s response to the discovery of these problems.

2. For a review of our work on stratospheric ozone depletion described in a review article in 1991, and in my 1995 Nobel Prize lecture published in 1996, see F. Sherwood Rowland, Stratospheric Ozone Depletion, 42 ANN. REV. PHYSICAL CHEMISTRY 731 (1991); F. Sherwood Rowland, Stratospheric Ozone Depletion by Chlorofluorocarbons (Nobel Lecture), 35 ANGEWANDTE CHEMIE 1786 (1996). We began measuring the atmospheric concentrations of methane in 1978, and soon found that they were increasing. During the 1980s, the rise in methane became recognized as second only to the increase in carbon dioxide as a cause of global warming. See Edward W. Mayer et al., Methane: Interhemispheric Concentration Gradient and Atmospheric Residence Time, 79 PROC. NAT’L ACADEMY SCI. 1366 (1982) for our first reported measurements. Our studies of smog are illustrated by our investigations of the air in Mexico City, and the discovery that liquefied petroleum gas (LPG) is an important contributor to smog in that city, as described. See Donald R. Blake & F. Sherwood Rowland, Urban Leakage of Liquefied Petroleum Gas and Its Impact on Mexico City Air Quality, 269 SCI. 953 (1995).
Stratospheric ozone depletion, global warming, and smog involve very different processes but have important similarities. Each involves changes in the trace gas composition of the atmosphere, and the mixing of the trace gases via wind patterns eventually causes them to interact with one another. In addition, I want to make it clear that ozone depletion, global warming, and smog are fundamentally concerned with three different aspects of the atmosphere. However, because they are occurring simultaneously in the only atmosphere we have, inevitably there are some cross-interactions.

Stratospheric ozone depletion is a process that allows more solar ultraviolet radiation to penetrate to Earth's surface because ozone is the primary agent of absorption for incoming ultraviolet radiation, especially in the so-called UV-B range with wavelengths between 280 and 320 nanometers (nm). \(^3\) Global warming is the consequence of increasing absorption of outgoing terrestrial infrared radiation by trace atmospheric components such as carbon dioxide, methane, and nitrous oxide. In short, the former is about weakening of the atmospheric shield against incoming ultraviolet radiation, and the latter is about making the escape path for outgoing infrared radiation more difficult. Photochemical smog is the formation of too much ozone at the surface of the Earth; the ozone accumulates because of the combined interaction of sunlight with hydrocarbon and nitrogen oxide pollutants released by human activities, usually by automobiles.

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3. The electromagnetic spectrum includes visible radiation with wavelengths varying from 740 nm (red light) to 380 nm (violet light), plus the invisible portions greater than 740 nm (infrared, or IR radiation) and less than 380 nm (ultraviolet, or UV radiation). The boundaries of these wavelengths are not sharp (often listed as 700 nm (red) to 400 nm (violet)) because the radiation detection capability of the human eye gradually fades out at both boundaries. The individual energies of radiation are inversely proportional to the size of the wavelength, with the most energetic in the short wavelength UV. The UV spectrum itself is often divided into UV-A between 320 to 380 nm, most of which passes through the atmosphere and reaches the Earth's surface and its inhabitants; UV-B between 280 to 320 nm, some of which reaches the surface and some of which ozone absorbs in the stratosphere; and UV-C, with wavelengths less than 280 nm, none of which reaches the surface because of absorption by ozone and by molecular oxygen in the atmosphere. The primary deleterious effects of UV radiation on humans (for example, skin cancer) are caused by UV-B radiation because these wavelengths can be absorbed by DNA in the skin, inducing defects. Everyone constantly receives UV-A as part of sunlight, and humans have evolved not to be strongly affected by this exposure. Absorption of UV-C radiation can also be quite deleterious to humans, but exposure does not occur through sunlight because UV-C radiation is removed in the stratosphere. Even with any presently conceivable depletion of stratospheric ozone, UV-C will continue to be absorbed in the stratosphere.
A. Discovery of the Problem

I completed my doctoral work, long ago, in the field of radiochemistry—the chemistry associated with radioactive isotopes and especially the chemistry in the immediate aftermath of a nuclear reaction that creates the radioactive isotope. An important aspect of radiochemistry is that the chemical species in question are present in ultraminate, or trace quantities, and all measurements require extremely sensitive analytical techniques. My mid-career expansion into research outside the laboratory—that is, into environmental studies—came primarily from simple curiosity about the behavior of some trace species after their release into the environment. A significant crossover from my earlier work is that many of the most important chemical processes in the atmosphere involve chemical entities present in exceedingly small quantities, again requiring very specialized instruments. Moreover, in addition to the severity of the analytical requirements, the parallel thought patterns of chemical concern for widely different trace species are not those applicable to changes involving the major components. A very large number of collisions with bulk molecules intervene between successive collisions of one trace species with another, whereas bulk molecules keep hitting each other all of the time. In the atmosphere, almost all of the collisions with nitrogen, oxygen, argon, and carbon dioxide are just that—hundreds of millions of successive collisions with no accompanying chemical change.

I was fortunate, between 1970 and 1974, to be conducting research under the auspices of a U.S. governmental agency—the Atomic Energy Commission (AEC)—that allowed its Principal Investigators ("the contract PI") considerable freedom in choosing which chemical systems they would study. Early in 1972, at a Chemistry/Meteorology Workshop convened by the AEC in Fort Lauderdale, Florida, I learned of some experiments by a British

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5. One contributory reason why nitrogen (78%), oxygen (21%), and argon (0.9%) are abundant in the atmosphere is that nothing happens to them very quickly. The reactive chemicals go away rapidly and they do not accumulate into major amounts. The characteristics of the atmosphere are described in many places. E.g., RICHARD P. WAYNE, CHEMISTRY OF THE ATMOSPHERE (2nd ed. 1991).
scientist, Jim Lovelock, who had invented and built a homemade device that improved the sensitivity of detection in the atmosphere about one million-fold for certain compounds, specifically those with a strong affinity for electrons. Among these "electron-capture" compounds are many synthetic molecules, not present in the natural environment, which have two or more chlorine or bromine atoms.

With his instrument, Lovelock established that CCl$_3$F, a member of the chlorofluorocarbon or CFC family of compounds, was present in both the northern and southern hemispheres at levels of about fifty parts in $10^{12}$. This CFC is one of a class of compounds first synthesized seventy years ago in the search for a non-reactive, non-toxic, odor-free refrigerant. All major CFC uses (refrigerant, propellant gas for aerosols, air-conditioner fluid, cleaning solvent, etc.) rely heavily on CFC's lack of chemical reactivity, and almost all CFCs are eventually released unchanged into the atmosphere during or after use.

Here was a compound, deliberately designed to be very chemically unreactive, now found to be accumulating in the atmosphere. I became curious about its eventual atmospheric fate and I asked myself the general question, "Do we know enough about the behavior of these molecules from laboratory experiments to predict what will happen to them when set loose in the environment?" Early in 1973, I submitted my annual contract renewal proposal to the AEC and included a short section in which I requested some additional funding to allow

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6. The correct chemical name for CCl$_3$F is trichlorofluoromethane but it is usually industrially identified as CFC-11, or Freon-11 using the trademark of the DuPont Company. This numbering system is an arcane special code created long ago for the commercial applications of chlorofluorocarbon compounds. A three-digit number identifies each compound. The first digit is the number of carbon atoms minus one, the next digit is the number of hydrogen atoms plus one, and the last is the number of fluorine atoms. By this code, CCl$_3$F is CFC-011 and the zero is then omitted. Other technologically important CFC compounds are CCl$_2$F$_2$ (CFC-12), CClFCClF$_2$ (CFC-113), and CHClF$_2$ (known in the 1970s as CFC-22, and redesignated as HCFC-22 when it became desirable from a regulatory perspective not to be a CFC—the hydrogen atom provides a much shorter atmospheric lifetime and puts it in a less stringently regulated class). Anyone finding a rational reason for the invention and adoption of this code (and its ramifications not included here) is then invited to provide a rational explanation for the correct English pronunciation of the following words: though, through, thought, rough, slough, and Leicester.


investigation of the fate of the chlorofluorocarbons in the atmosphere. The AEC responded that the financial level of my contract was already fixed for the following year, but I was free to allocate the funds among the various topics discussed in the proposal, including, if I so chose, the fate of CFCs.\(^9\)

Our study of the atmospheric fate of CFCs began in October 1973 when Dr. Mario Molina—now a University Professor at the Massachusetts Institute of Technology—joined my research group as a Post-Doctoral Research Associate. He elected to work on the atmospheric fate of the CFCs from a short list of possible topics. The study began as a scientific question about the environment, but it was not an environmental "problem" in the sense of an investigation whose results could cause concern among laymen, potentially requiring regulations or even remedial actions. The first steps of the study were simply an evaluation of the likelihood of possible processes—sinks—that might chemically remove CFCs from the troposphere,\(^10\) the lowest part of the atmosphere.

By late November, we had determined that near-surface sinks failed to provide any significant process for reducing CFC levels in the troposphere. The common atmospheric reactions for most chemicals include absorption of solar radiation with subsequent molecular decomposition, dissolution in raindrops, or reaction with oxidizing components of the atmosphere such as molecular oxygen, ozone, or the hydroxyl radical (HO). But CFCs are transparent both to visible radiation and to the UV radiation

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9. I think this permission illustrates an agency research management strategy that is much less frequently found now in our federal (or state) government. Requirements for judging the quality of a research idea (and whether it should be funded) now rest almost entirely on the desirability of the anticipated outcome and the likelihood of achieving it. In 1973, I was in the seventeenth year of consecutive support from the AEC. Past research productivity in the AEC's view allowed it to consider proposed projects whose end result and significance was not already known and therefore could not be accurately evaluated in advance. The AEC program officer recognized the possibility that something important, even though unforeseen, might come out of truly exploratory experiments.

10. The troposphere, which contains about ninety percent of the atmosphere's molecules stretches from the surface up to the tropopause, defined as the altitude at which the temperature no longer decreases with increasing height. The tropopause lies about five miles above the surface in the polar regions, increasing to ten miles in the tropics. The stratosphere extends from the tropopause to an altitude of thirty miles, where the temperature begins to fall again with increasing altitude, and it contains about ten percent of the atmosphere. Only about 0.1 percent of the atmosphere's molecules exist at altitudes higher than thirty miles.
that reaches the lower atmosphere ("near-UV"), are insoluble in water, and do not react with the common oxidizing agents.\textsuperscript{11}

This conclusion meant that CFCs should survive for many decades in the atmosphere because nothing happens to them in the ninety percent of Earth's atmosphere into which they mix initially. The CFC molecules are able to absorb short wavelength ultraviolet (the more energetic end of UV-C), but at altitudes of twelve to twenty-five miles, ozone intercepts all such solar UV-C radiation. The individual CFC molecules drift randomly through the atmosphere for many decades and eventually wander up far enough—above most of the stratospheric ozone—to encounter UV-C radiation. The internal release of this energy is sufficient to destroy the CFC molecule, breaking it into a chlorine atom and a radical fragment, as shown in equation (1) for $\text{CCl}_3\text{F}$:\textsuperscript{12} We performed a calculation which indicated that the average lifetime of $\text{CCl}_3\text{F}$ in the atmosphere would be about forty to eighty years, while that of its even more widely used companion molecule, $\text{CCl}_2\text{F}_2$ (CFC-12), would be about eighty to 150 years.

\begin{equation}
\text{CCl}_3\text{F} + \text{UV} \rightarrow \text{Cl} + \text{CCl}_2\text{F}
\end{equation}

These were still answers to a series of scientific questions and no environmental "problem" had yet surfaced. Then, Molina and I asked the question, "What will happen to the chlorine atom?" Stratospheric ozone re-enters the discussion at this point. Very short wavelength solar UV radiation can be destructively absorbed by atmospheric oxygen, $\text{O}_2$, splitting it into two individual $\text{O}$ atoms, each of which usually finds another $\text{O}_2$ and combines with it to form the triatomic form of oxygen known as ozone, $\text{O}_3$. This ozone can in turn absorb additional solar UV radiation, splitting $\text{O}_3$ into $\text{O}$ plus $\text{O}_2$, followed immediately by the $\text{O}$ atom finding another $\text{O}_2$ molecule and reforming a very energetic ozone molecule. An important consequence of this reaction sequence is that subsequent collisions of this excited ozone molecule transfer the energy to other molecules, resulting in the eventual conversion of the absorbed solar UV energy into heat energy. This mid-

\textsuperscript{11} For a background on terms, equations, and processes mentioned in this section of this Article see \textit{supra} note 2; \textit{WAYNE}, \textit{supra} note 5; Rowland & Molina, \textit{supra} note 8. A series of six very comprehensive international reports for the scientific community have been issued by the World Meteorological Organization, beginning in 1986. For the most recent of these reports, see WMO Report, \textit{infra} note 57.

\textsuperscript{12} The $\text{CCl}_3\text{F}$ radical fragment in equation (1) reacts almost instantly with molecular oxygen, and the cascade of subsequent chemistry releases the other chlorine atoms, too.
atmospheric heat source creates the stratosphere, the region of the atmosphere in which the temperature rises with increasing altitude. Ozone, however, is itself quite chemically reactive and can be removed by a series of natural chemical reactions, maintaining a steady balance in the stratosphere. The interconnection between CFCs and ozone is therefore not accidental—CCl₃F and O₃ compete for the same solar UV radiation. The CCl₃F molecule is protected from UV radiation by the ozone above it until the molecule has risen to high altitudes—about fifteen to eighteen miles—a height above much of the ozone layer.¹³ Unlike its parent CCl₃F, the chlorine atom from reaction (1) is extremely reactive and initiates chemical changes as soon as it emerges into the stratosphere.

Within one second, the chlorine atom from equation (1) reacts with an ozone molecule by reaction (2), forming another chlorine compound, the free radical CIO.¹⁴ The CIO, in turn, takes about one minute to react with atomic oxygen by reaction (3), releasing atomic chlorine once more. The net result of reaction (2) plus reaction (3) is conversion of one ozone molecule and one potential ozone molecule (the oxygen atom would have otherwise formed an ozone molecule) into stable atmospheric oxygen, shown by reaction (4). This combination leaves the chlorine atom fully ready to react again, which it does, wandering randomly up and down, undergoing a long series of chemical reactions until finally in a year or so it returns to the lower atmosphere. The sequence of reaction (2), plus reaction (3) comprises what is known as a free radical catalytic chain reaction—a series in which the catalysts (Cl and CIO) cause ozone reactions to occur rapidly but survive themselves to react over and over again.¹⁵

¹³. See Rowland & Molina, supra note 8, at 2 (providing measurements converted from km).

¹⁴. Much of chemistry is explained by the tendency of electrons to pair with one another, and chemical species with an odd number of electrons are very reactive and are designated as "free radicals." The chlorine atom has seventeen electrons, and the CIO radical has twenty-five electrons. Rowland & Molina, supra note 8. See also WAYNE, supra note 5, for a more general view.

¹⁵. This chain reaction was first discussed at a scientific meeting in Kyoto, Japan, in September 1973. For the published results of the Kyoto meeting, see R. S. Stolarski & R. J. Cicerone, Stratospheric Chlorine: A Possible Sink for Ozone, 52 CANADIAN J. CHEMISTRY 1610, 1610-615 (1974). Unaware of the Kyoto meeting, we independently discovered the chain reaction in November 1973 and published it in 1974. See Mario J. Molina & F. S. Rowland, Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom Catalysed Destruction of Ozone, 249 NATURE 810, 810-12 (1974). By the time both articles appeared, the respective authors were fully aware of the sequence of events. The chain reaction was discussed in more
The natural stratospheric removal processes for ozone are then supplemented by chlorine-based sequences such as those represented in equation (2) and equation (3). The average ozone molecule survives for a shorter time and less ozone is present than before. Each chlorine atom eventually removes about 100,000 molecules of ozone before finally drifting randomly down into the lower atmosphere, with removal as HCl dissolves in raindrops. The combination of a yearly global production of about one million tons of CFCs in the 1970s and 1980s with the large multiplying factor from the chain reaction puts the removal of ozone by chlorine on the same scale as the natural global processes for formation and removal of ozone.

An interesting scientific study had now been transformed into the genuine environmental problem known as stratospheric ozone depletion. By Christmas 1973, Molina and I knew that we had a bear by the tail and we submitted a short paper to the journal *Nature* the next month. This first paper came out in June 1974; our much longer comprehensive discussion of the detail in Rowland & Molina, *supra* note 8. See WAYNE, *supra* note 5, for a more general view.

16. The chemical form of the chlorine atom alternates among the free atom (Cl) and its chain reaction partner (ClO), but can be diverted by competing reactions into other chemical forms such as hydrogen chloride (HCl), chlorine nitrate (ClONO₂) and HOCI. The chlorine atom does not remove ozone while in these chemical forms, which act as "temporary reservoirs" outside the active chain removal of ozone. Other chemical reactions attack the reservoirs and once again release atomic chlorine, and the chain reaction begins anew. Measurements of the rate constants of the various chemical reactions over the temperature ranges occurring in the stratosphere have been a very important, continuing activity of the atmospheric chemical community.

17. The yearly global production rates of the different chlorofluorocarbons have been accumulated in a series of reports by the Chemical Manufacturers Association, and summarized in the national and international evaluations of the effects of chlorofluorocarbons in the atmosphere. For yearly production rates prior to 1974, see Rowland & Molina, *Chlorofluoromethanes, supra* note 8, at 4.

18. Molina & Rowland, *supra* note 15. Scientific communications of wide general interest are usually quickly published in brief reports and followed later with very many more details in other journals with more specialized interests. In practice, the two most widely used general interest scientific journals are *Science*, published by the American Association for the Advancement of Science, and *Nature*, published privately in London. See LYDIA DOTTO & HAROLD SCHIFF, THE OZONE WAR (1978) for a description by a professional science writer and a leading atmospheric scientist, respectively, of some of the vicissitudes in the publication of these papers.
atmospheric science associated with chlorofluorocarbon release was published in February 1975.19

B. Response to the Problem

In mid-1974, Molina and I publicly called for global regulation of the release of CFCs, especially in their use as propellant gases in aerosol sprays for hair, deodorants, etc.20 At that time, the United States accounted for about half of the world's CFC releases; aerosol sprays accounted for two-thirds of all U.S. use.21 Response to the initial formulation of the problem came within a few months. The first U.S. Congressional Hearing was held in December 1974;22 further hearings were held in Congress and in many states during 1975.23 The first regulation to take effect was signed into state law in Oregon on June 16, 1975, banning the use of CFCs as propellants in aerosol sprays.24 For the United States as a whole, discussion and argument occurred over which regulatory agency had jurisdiction and responsibility: the Consumer Product Safety

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24. See S. 771, 1975 Leg. Reg. Sess. (Or. 1975) (enacting regulations "prohibit[ing] [the] sale of aerosol spray containing certain chlorofluorocarbon compounds not containing hydrogen after March 1, 1977"). Of course, this action was largely symbolic because Oregon represented only a minuscule fraction of total global CFC usage. It did, however, make Oregon a very useful test market for industry evaluation of consumer response to delivery of specific products by different substitute methods, such as hydrocarbon propellant gases, finger-activated pump valves, and roll-on deodorants.
Commission (CPSC), the Food and Drug Administration (FDA), or the Environmental Protection Agency (EPA). 25

Meanwhile, ozone depletion began to receive independent confirmation from other scientists, spurring further government response, both in the United States and around the globe. First, the Committee on Inadvertent Modification of the Stratosphere (IMOS) representing 14 U.S. federal agencies, reported in June 1975 that the problem appeared to be quite legitimate. 26 Then, in September 1976, the National Academy of Sciences Panel on Atmospheric Chemistry issued a report entitled "Halocarbons: Effects on Stratospheric Ozone." 27 In October 1976, the EPA and the FDA announced a federal prohibition, to take effect eighteen months later, on the use of CFCs as aerosol propellants. 28 Canada and several Scandinavian countries also put aerosol propellant regulations into effect in the late 1970s. 29

The rest of the world did not immediately follow suit. After this first phase of regulation, confined to controlling the use of CFCs as aerosol propellants in several countries, discussions of further regulations died down until the mid-1980s. In the United States there was a widespread public belief that the "CFC problem" was only an aerosol propellant problem and that it had


27. PANEL ON ATMOSPHERIC CHEMISTRY, NAT'L RESOURCE COUNCIL, HALOCARBONS: EFFECTS ON STRATOSPHERIC OZONE (1976) (for a shorter, broader look see COMMITTEE ON IMPACTS OF STRATOSPHERIC CHANGE, NAT'L RESOURCE COUNCIL, HALOCARBONS: ENVIRONMENTAL EFFECTS OF CHLOROFLUOROMETHANE RELEASE (1976)). See also Harvey Brooks, Stratospheric Ozone, the Scientific Community and Public Policy, in STRATOSPHERIC OZONE AND MAN, supra note 25, at 201, for a discussion of the entire situation at the time of the National Academy of Sciences deliberation.

28. See Demise of Aerosol Can Is in Sight as U.S. Moves to Phase Out Fluorocarbon Sprays, WALL ST. J., Oct. 18, 1976, at 2. The story describes coordinated activities by the Food and Drug Administration, the Consumer Product Safety Commission, and the Environmental Protection Agency to phase out all non-essential uses of CFCs as aerosol propellants within the next two years. (The headline is quite inaccurate because the activities affected only the use of CFCs as propellants, and left other aerosol can uses undisturbed).

29. The article by Carroll Leslie Bastian contains a short summary of the specific chlorofluorocarbon regulatory actions of various individual countries during the late 1970s to 1981, prior to more general agreement on unified international control mechanisms. See generally Bastian, supra note 26.
been solved by the regulations already in place.\textsuperscript{30} In contrast, the prevailing belief in Europe and Japan was that there was no real environmental problem associated with the CFCs, and therefore they were satisfied because no CFC regulations were required in their countries.\textsuperscript{31}

Inevitably, expanded scientific scrutiny questioned and challenged various aspects of the existing formulation of what was now described as the CFC-Stratospheric Ozone Depletion problem. Our calculations in 1974 indicated that the ratio of $\text{CCl}_3\text{F}$ to $\text{N}_2$ and $\text{O}_2$ in the atmosphere would remain constant throughout the troposphere (although the concentration of each of them would decrease by a factor of ten for a nine mile increase in altitude), and then the ratio would begin to fall off rapidly with increasing altitude in the lower stratosphere. Little $\text{CCl}_3\text{F}$ would survive above an altitude of eighteen miles.\textsuperscript{32} We made this prediction before anyone had taken measurements of any chlorine-containing molecule in the stratosphere. Especially common were the frequent comments made about the unlikelihood or even impossibility of the heavier-than-air CFCs rising into the stratosphere. After all, others argued, the molecules of both $\text{CCl}_3\text{F}$ and $\text{CCl}_2\text{F}_2$ are more than four times as heavy as the $\text{N}_2$ and $\text{O}_2$ molecules that make up 99% of the air.\textsuperscript{33}

\textsuperscript{30} The range of beliefs also went far beyond thinking the CFC problem had been solved with the regulation of their use as aerosol propellants. See ANNE BURFORD, ARE YOU TOUGH ENOUGH 133 (1986), in which the author described the events during her turbulent years (1981-1983) as the first administrator of the Environmental Protection Agency in the Reagan administration and stated, "the acid rain problem has become an even bigger issue since I was in office. Putting aside for the moment that it has become the scare issue of the day—remember a few years back when the big news was fluorocarbons that supposedly threatened the ozone layer?—acid rain does represent a serious environmental as opposed to a health hazard."

\textsuperscript{31} For example,

in the United Kindgom and France, whether justified or not, many believe that the environmental objections to supersonic transport were bogus, inspired by chauvinism in the United States, and were specifically anti-Concorde. Consequently, instead of a sensitization towards the idea of ozone depletion, the very reverse has occurred in these countries. . . . But the preference for prejudice over evidence persists. In such a public environment where stratospheric ozone is a sacred thing, the chlorofluorocarbons never stood a chance; the moment they were suspected, and later in theory, it seems as if in the United States even holy water would be banned if it were suspected of depleting ozone.


\textsuperscript{32} E.g., supra note 8.

\textsuperscript{33} See CHEM. MKTG. REP., Sept. 30, 1974, at 3 (describing how "Dr. [Oliver C.] Taylor questions the basic hypothesis of the ozone breakdown theory— that inert
In 1975, two separate research groups sent balloon-borne evacuated containers into the stratosphere with pressure sensors set to open at chosen altitudes. Both groups confirmed that: (1) the CFCs did indeed penetrate readily into the stratosphere; and (2) the CFCs did disappear at the predicted altitudes for $\text{CCL}_3\text{F}$ and $\text{CCL}_2\text{F}_2$.\textsuperscript{34} Despite these observations and numerous subsequent studies on CFCs in the stratosphere, claims still appear decades later that the CFCs are unable to reach the stratosphere because they are much heavier than air.\textsuperscript{35}

C. The Antarctic Ozone Hole and Global Action

The next major development relative to ozone depletion was the discovery, in 1985, of a massive loss of ozone every spring fluorocarbon gases rise slowly to the stratosphere where ultraviolet light decomposes them releasing chlorinating to damage the ozone.


35. See Rogelio Maduro & Ralf Schauhammer, The Holes in the Ozone Scare 102 (1992) (stating in a quotation from climatologist Robert Pease that, "It is precisely because they are so much heavier than air... that it takes considerably more eddy turbulence to support and move the molecules upward through this thermal barrier of the stratospheric inversion than other, lighter air gases. With the insufficient eddy motion that exists at the base of the stratosphere, there will be a gravity bias in the supporting eddy turbulence that causes the net exchange of molecules across the tropopause barrier to have downward bias. This provides a slow-acting sink for stratospheric CFCs that matches the slow percolation upward through the inversion thermal barrier."); see also Dixy Lee Ray, Environmental Overkill 35 (1993) (considering the question: "How does CFC rise when its molecules are four to eight times heavier than air? All experience with freon and related CFCs shows that they are non-volatile and so heavy that you can pour CFCs from a container and if some of them spill, they will collect at the lowest point on the ground, where soil bacteria will decompose them. Of course, some molecules will be caught in upward air eddies or otherwise carried upwards, but this is a very small fraction of the total.").

At this point, I will interject a comment about why the CFC problem is quantitatively different from most environmental problems: anybody, anywhere has free access to the atmosphere and can do experiments on its composition. The winds move the air and everything in it worldwide, so that globally significant data can be recorded far from the point of emission into the atmosphere. Legal permission is not required. Just go outside, take an air sample, and look for CFCs or another compound of interest. (This may not be true for investigations of photochemical smog in urban environments of different nations, although even then you can wait downwind to capture an air sample.) Because of this easy access and the global nature of the resulting problem, many more than 10,000 scientific papers have been published in the past 25 years that are closely related to the problem of stratospheric ozone depletion. There is absolutely no shortage of data here.
over Antarctica—the "Antarctic ozone hole."\textsuperscript{36} The initial report came from a ground-based British Antarctic Survey (BAS) station at Halley Bay, established on the Antarctic coast at 75.5 degrees south latitude.\textsuperscript{37} The BAS started taking measurements of total ozone overhead in 1956, and it has continued ever since. By 1984, the BAS reported that the average amount of ozone overhead during the month of October had decreased by 35 percent from the values characteristic of the 1960s.\textsuperscript{38} The NASA Nimbus-7 satellite quickly confirmed these data, showing that ozone loss was not narrowly confined to the Halley Bay region but rather covered ten million square miles, an area more than three times as large as the continental United States.\textsuperscript{39} In succeeding years, the Nimbus-7 data registered continuing ozone depletion until losses of 70 percent were being recorded over parts of Antarctica by 1990.\textsuperscript{40}

In the late spring (the last half of November), Antarctic meteorology changes drastically and the stratospheric air mass—now depleted in ozone during September—that has been over the polar region since May is fragmented and displaced northward by ozone-richer air coming in from the temperate latitudes. At this time, Antarctic measurements indicate that ozone returns to more normal values, while data from some stations in the temperate latitudes exhibit decreased ozone levels as portions of ozone-depleted, northward moving air from Antarctica mix into the air already there.\textsuperscript{41}


\textsuperscript{37} The countries of the world agreed to a combined, comprehensive international geophysical study called the International Geophysical Year, or IGY, which actually lasted for eighteen months from July 1957 through December 1958. Two of the programs initiated during the IGY were the BAS study of ozone over Antarctica and C. David Keeling's measurement of the atmospheric concentrations of carbon dioxide at Mauna Loa (Hawaii) and the South Pole, which is discussed later in this Article. These long-term, highly accurate records have been very important in establishing that the loss of ozone and the increase in carbon dioxide, respectively, are real changes and not just normal variability.

\textsuperscript{38} See Farman, supra note 36, at 208.


\textsuperscript{40} The data showing the measured amounts of ozone over the southern hemisphere are available at NASA's website on a day-by-day basis for the fourteen-plus years (November 1978-May 1993) of operation of the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus-7 satellite, and for the TOMS instruments on other satellites since that time. See NASA, \textit{Total Ozone Mapping Spectrometer, available at} http://jwocpy.gsfc.nasa.gov/TOMSmain.html.

\textsuperscript{41} The measured ultraviolet exposure for humans living in New Zealand increased by 12 percent during the decade of the 1990s because of the steady loss of stratospheric ozone in the southern hemisphere. Richard McKenzie et al., \textit{Increased
Several U.S. expeditions established the cause of this intense loss of ozone over Antarctica. The first was a 1986 ground-based study at McMurdo, Antarctica, which indicated that the ozone losses were induced by unusual chemistry, much of it involving the chlorine-containing free radical, ClO.\textsuperscript{42} Subsequent experiments in 1987, both at McMurdo and with aircraft flying over Antarctica from a base in Punta Arenas, Chile, established conclusively that chlorine atoms, set free by the arrival of sunlight after the long polar darkness, played the dominant role in rapidly removing stratospheric ozone.\textsuperscript{43} The most significant chlorine chain processes in the polar stratosphere follow a different path than the one outlined earlier because the oxygen atoms needed for reaction (3) are much less abundant in the early polar spring than they are in the tropical and temperate mid-stratosphere. Instead, the dominant polar sequence involves the combination of two ClO radicals to form the chlorine oxide dimer, ClOOC1, which is then decomposed by light into two chlorine atoms and an O\textsubscript{2} molecule.\textsuperscript{44}

Earlier symposium articles discuss the Montreal Protocol. The countries of the world, under the auspices of the United Nations Environment Program, created the framework Vienna Convention for Protection of the Ozone Layer in March 1985.\textsuperscript{45} In September 1987, the parties to the Convention agreed to enact actual controls on ozone-destroying chemicals through the Montreal Protocol on Substances that Deplete the Ozone Layer.\textsuperscript{46} Regulations were scheduled to become effective a decade later to

\textit{Summertime UV Radiation in New Zealand in Response to Ozone Loss.} 285 Sci. 1709, 1709 (1999). The measuring equipment for ultraviolet radiation was not in place during the 1980s when ozone loss also occurred.


\textsuperscript{43} J. G. Anderson et al., Kinetics of Ozone Destruction by ClO and BrO Within the Antarctic Vortex: An Analysis Based on in situ ER-2 Data, 94 J. Geophysical Res. 11,480 (1989).

\textsuperscript{44} L. T. Molina & M. J. Molina, Production of Cl\textsubscript{2}O\textsubscript{2} from the Self-reaction of the ClO Radical, 91 J. Physical Chemistry 433, 435 (1987).

\textsuperscript{45} Richard E. Benedick describes in detail the negotiations leading to the Vienna Convention and the Montreal Protocol. See Richard E. Benedick, Ozone Diplomacy: New Directions in Safeguarding the Planet (enlarged ed. 1998). The full wording of the agreements is contained in the Appendices. \textit{Id.} at app. This book is, however, almost entirely concerned with the progress of international negotiations in the period after 1985, with almost no discussion of the national regulatory efforts during the preceding decade.

\textsuperscript{46} \textit{Id.} at chs. 7-8.
reduce CFC emissions to fifty percent of 1986 levels. Meeting in mid-September 1987, the parties agreed that, for the purposes of the negotiations in Montreal, the cause of the Antarctic ozone losses would be assumed as unknown, but everyone knew that these massive losses were occurring again even as they met, that the previous year's expedition had placed the blame on artificial chemicals, and that two well-equipped expeditions were in the middle of studies likely to show conclusively the connection to CFCs.

The Vienna Convention of 1985 included procedures for regularly revisiting the stratospheric ozone situation to determine whether more regulation was required. In March 1988, the NASA-WMO Ozone Trends Panel reported that (a) the chlorine atoms released from CFCs were the primary cause of the Antarctic Ozone Hole; and (b) significant winter-time ozone losses had already been recorded by ground stations in the United States, Europe, and Japan. At this juncture, the

47. Id. at 355.

48. The question of whether the Antarctic Ozone Hole played an important role in Montreal has some importance relative to the Precautionary Principle—whether control actions should be taken in advance of clear evidence of damage if the risks are judged to be too high. The pure Precautionary Principle position here requires that the participants believed that the Ozone Hole was merely a recently discovered natural phenomenon; a slightly less pure position would be that it might be either natural or induced by the activities of mankind.

R. Grundmann has extensively interviewed about fifty of the participants most closely involved in ozone science and policy, and he has quoted extensively (in almost all quotations, the speaker is not identified by name) from them in his book. See REINER GRUNDMANN, TRANSNATIONAL ENVIRONMENTAL POLICY: THE OZONE LAYER (forthcoming Mar. 2001). Grundmann has pointed out that videos of the progression of the ozone hole were shown at the meeting in Montreal. Id. at 180. He also says, "Everyone questioned in my investigation (except for the defenders of the official version) admits that the Antarctic Ozone Hole was absolutely crucial in reaching their compromise. . . ." He also quotes one of the major participants (not identified) in Montreal as saying, "But, when it was documented that ClO was really existing in enormous big amounts in the vortex, then things started to fit together." Grundmann then continues, "At the mention of the official version, claiming that the ozone hole played no role at Montreal, this interviewee replied, 'Bullshit!'" Id.

49. See BENEDICK, supra note 45, at 344, 359 (asserting that, "[t]hereafter, ordinary meetings of the Conference of the Parties shall be held at regular intervals to be determined by the Conference at its first meeting" and that "[b]eginning in 1990, and at least every four years thereafter, the Parties shall assess the control measures provided for in Article 2 on the basis of available scientific, environmental, technical and economic information.") (quoting the Vienna Convention, art. 6 and the Montreal Protocol, art. 6).

DuPont Company, the world’s largest manufacturer of CFCs, abruptly announced its decision to stop as rapidly as possible further production of CFCs.\textsuperscript{51} The announcement came ten days after the Panel report that the scientific evidence on the effects of CFCs on the ozone layer was now persuasive.\textsuperscript{52}

With industry resistance to further regulation now collapsing, the parties to the Montreal Protocol met again in London in 1990, this time raising the 50 percent cutback to a 100 percent ban, again effective by 1999.\textsuperscript{53} A subsequent meeting in Copenhagen in 1992 moved the effective date of the 100 percent cutback forward to January 1, 1996, slightly more than four years ago.\textsuperscript{54} In all of these negotiations, the developing countries were allowed a one-decade regulatory delay in order not to forestall expansion of essential processes such as refrigeration of food.\textsuperscript{55} The practices of developed, affluent societies, however, had accounted for the major high-volume uses of CFCs and the delayed ban for developing countries played a very minor role in total CFC emissions.\textsuperscript{56}

Everyone can now readily observe that the Montreal Protocol has been a major success. Measurements in the atmosphere itself have shown that the global atmospheric concentration of CCl\textsubscript{3}F—the molecule whose fate Molina and I first contemplated in 1973—peaked about 1995 and has been slowly decreasing ever since.\textsuperscript{57} The atmosphere itself has delivered the verdict. The.


52. See supra note 50.

53. BENEDICK, supra note 45, at ch. 13.

54. Id. at ch. 14.

55. Id. at 358.

56. The global manufacture of CFCs has been carried out by approximately twenty companies, of whom perhaps ten, all situated in the developed countries, were responsible for about ninety-five percent of world production. Most of the detailed evaluations of such contributions were issued in technical reports from groups such as A. D. Little and the Rand Corporation, or by the Manufacturing Chemists Association (later the Chemical Manufacturers Association) Technical Panel. For a general description of the global enumeration process see J. Peter Jesson. Halocarbons, in STRATOSPHERIC OZONE AND MAN, supra note 25, at 29; A. McCulloch et al., Distribution of Emissions of Chlorofluorocarbons (CFCs) 11, 12, 113, 114, and 115 Among Reporting and Non-Reporting Countries in 1986, 28 ATMOSPHERIC ENV’T 2567 (1994).

total amount of organochlorine compounds contained there is now decreasing. Because of the long atmospheric lifetimes of the CFCs—about fifty years for CCl$_3$F and 100 years for CCl$_2$F$_2$—significant amounts of these compounds will still be in the atmosphere in the year 2100. For CCl$_2$F$_2$, the present concentration of 540 parts per trillion (pptv) by volume is expected to decrease to 200 pptv in 2100, 70 pptv in 2200, and 25 pptv three centuries from now.\textsuperscript{58} In addition, the atmospheric concentration of one chlorine-containing compound, methylchloroform (CH$_3$CCl$_3$), has declined much more precipitously since being banned under the Montreal Protocol because the presence of C-H chemical bonds in this molecule allows it to be oxidized in the atmosphere by reacting with an HO radical, as shown in equation (5).\textsuperscript{59} The measured atmospheric concentration of methylchloroform has now fallen to about forty percent of its 1994 level.\textsuperscript{60}

\begin{equation}
\text{HO} + \text{CH}_3\text{CCl}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CCl}_3
\end{equation}

The World Meteorological Organization has issued a series of comprehensive scientific evaluations of ozone depletion since 1986. In Chapter One, measurements showed that the total tropospheric burden of carbon-bonded chlorine (chiefly CFCs, carbon tetrachloride, methylchloroform and methyl chloride) went through a maximum in about 1994. The yearly release of CFCs and methylchloroform tapered off sharply in the early 1990s.

\textsuperscript{58} This calculation is simply the exponential loss on the basis of a 100-year lifetime. (Atmospheric scientists usually define the lifetime of a molecule as the average time a large group of such molecules survive in the atmosphere before being removed. Nuclear scientists usually use the term half-life, the time for half of the radioactive atoms to decay. A molecule with a 100-year lifetime corresponds to a half-life of 69 years). The underlying assumption of no major change in the operation of the atmosphere over the next three centuries is an unlikely one, but the point is that "business as usual" means that easily measurable quantities of CCl$_2$F$_2$ will be present for a very long time. Because the lifetime of CFCs in the atmosphere is controlled almost entirely by the structure of the stratospheric ozone layer and the rates of vertical mixing within the stratosphere, only a major change in one or both of these could change the atmospheric lifetime by as much as ten percent.

\textsuperscript{59} For the first description of the importance of attack on hydrogen attached to carbon as a major removal process in the lower atmosphere, see Sherry Rowland, \textit{Aerosol Sprays and the Ozone Shield}, 64 NEW SCIENTIST 717 (1974). For an evaluation of the utility of the atmospheric concentration of methylchloroform for calibration of the lifetimes of proposed substitute molecules for CFCs, see Yoshihiro Makide & F. Sherwood Rowland, \textit{Tropospheric Concentrations of Methylchloroform, CH$_3$CCl$_3$, in January 1978 and Estimates of Atmospheric Residence Times for Hydrocarbons}, 78 PROC. NAT'L. ACADEMY OF SCI. 5933, 5934 (1981).

\textsuperscript{60} Measurements into the year 2000 from unpublished data of D. R. Blake & F. S. Rowland (on file with author). See information infra note 73.
GLOBAL WARMING

A. Increasing Carbon Dioxide Concentrations in the Atmosphere

I will now turn my attention to the trace atmospheric gases most closely associated with the problem of global warming. In 1824, the French scientist Fourier formulated the principle that incoming solar radiation in the visible wavelengths ("the light rays") is balanced by outgoing terrestrial energy being emitted in invisible infrared wavelengths ("the dark rays"). He originated the current "greenhouse" terminology by comparing the action of the atmosphere to a "hothouse," the word used seventy-two years later in translation from the French to the English.

Seven decades after Fourier, the Swedish Nobelist-to-be Svante Arrhenius, well aware of the increasing use of coal and oil, calculated the warming effect of carbon dioxide in the atmosphere, with numerical results rather similar to those of the present day models. From time to time, too, atmospheric measurements were made of carbon dioxide concentrations, but detection of significant change requires accurate recordings over an extended period of time in many places, or in a very favorable particular site. These measurements, however, were neither well coordinated in location nor well calibrated instrumentally; thus the question of whether carbon dioxide concentrations were increasing was still uncertain.

Quantitative knowledge became available as the consequence of C. D. Keeling's establishment of two permanent monitoring stations for atmospheric carbon dioxide: one at Mauna Loa, Hawaii and the other at the South Pole. Within three years, the south polar data indicated a rising concentration of atmospheric carbon dioxide. Confirmation of this conclusion


64. Charles D. Keeling et al., *Atmospheric Carbon Dioxide Variation at the South Pole*, 28 TELLUS 552, 560 (1976) (elaborating on carbon dioxide increase reported in
took somewhat longer at Mauna Loa because northern hemispheric carbon dioxide concentrations vary much more widely during the year than do the concentrations in the south.\textsuperscript{65} Carbon dioxide concentrations vary because, while plant material decomposes and releases carbon dioxide year round, photosynthesis by green plants only occurs during the growing seasons of spring and summer, thus producing a net withdrawal of carbon dioxide from the atmosphere and fixing it into the flourishing vegetation.\textsuperscript{66} After this seasonal draw-down, which begins in spring and ceases at the end of the growing season, the level of carbon dioxide in the atmosphere then rises steadily during the succeeding autumn and winter. The Antarctic seasonal fluctuation is much smaller than in the northern hemisphere because most green plants grow on the land masses of the north, and north-south transfer of air between the hemispheres requires more than one year.

After a few seasons, the measurements clearly showed that this seasonal pattern of oscillating concentrations is superimposed on a rising background of carbon dioxide such that the yearly average concentration increased almost one part per million by volume (ppmv) per year over the 1958 yearly average of 315 ppmv.\textsuperscript{67} The primary cause of this rising carbon dioxide concentration is the burning of the fossil fuels, coal, gas, and oil.\textsuperscript{68} These fuels are designated as "fossil" ("dug up") because they are the buried residues of biological growth and death hundreds of thousands of years earlier. As explained earlier in the Article, the concept of global warming depends upon increased interference with the escape of outgoing terrestrial infrared radiation by the accumulation in the atmosphere of additional quantities of trace gases such as

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\textsuperscript{65} Charles D. Keeling, \textit{The Concentrations and Isotopic Abundance of Carbon Dioxide in the Atmosphere}, 12 \textit{TELLUS} 200, 203 (1960).

\textsuperscript{66} Charles D. Keeling et al., \textit{Atmospheric Carbon Dioxide Variations at Mauna Loa Observatory, Hawaii}, 28 \textit{TELLUS} 538, 546 (1976). The scientific details are now being evaluated periodically by the Intergovernmental Panel on Climate Change. See \textit{WORKING GROUP ONE, INTERGOVERNMENTAL PANEL OF CLIMATE CHANGE, CLIMATE CHANGE 1995: THE SCIENCE OF CLIMATE CHANGE} (1996) [hereinafter IPCC].

\textsuperscript{67} Keeling et al., \textit{supra} note 64, at 554.

\textsuperscript{68} IPCC, \textit{supra} note 65, at 14.
carbon dioxide. We have come a long way since Fourier. We now have an excellent quantitative understanding of how the wavelengths of radiation emitted by bodies, such as the sun and the Earth, depend upon their surface temperatures, with shorter wavelengths and higher energy intensities associated with hotter surfaces.\textsuperscript{69} The surface of the sun is approximately twenty times as hot as that of the Earth, and the peak solar wavelength, around 500 nm, is twenty-fold less than the peak wavelength from Earth at ten microns.\textsuperscript{70} The energy intensity per square inch of surface for solar emissions is about 160,000 times (that is twenty to the fourth power) that of the Earth. Earth emits infrared wavelengths, some of which match the absorption characteristics and capabilities of atmospheric molecules containing three or more atoms. Their characteristic infrared spectra—often called a molecular "fingerprint"—have strong absorptions at some specific wavelengths and transparency at many others in between. The important atmospheric gases in this region, the "greenhouse gases," include carbon dioxide ($\text{CO}_2$), water vapor ($\text{H}_2\text{O}$), nitrous oxide ($\text{N}_2\text{O}$), methane ($\text{CH}_4$), ozone ($\text{O}_3$), $\text{CCl}_2\text{F}$ (CFC-11), and $\text{CCl}_3\text{F}_2$ (CFC-12), among others.\textsuperscript{71}

In 1977, I realized that the research group needed accurate information about the concentrations of some of the chlorine-containing gases in a number of remote locations around the world—and this information was not being collected in the form we needed by any of the other research groups working in field measurements. So, in early 1978, we started a program of collection of air samples in coastal areas from Alaska to Punta Arenas at the southern tip of Chile. With these air samples, we first established an analytical system for measuring the concentrations of CFCs and some other chlorinated molecules, using a more advanced version of the system pioneered by

\textsuperscript{69} Such temperature-sensitive radiation is also emitted by humans, animals, trees, rocks, water, etc. Night vision goggles for the detection of human beings depend upon the higher intensity of infrared emission from human skin warmer than the surrounding materials and plants, and they do not work well in 100 degree heat, when the surroundings and humans are at similar temperatures.

\textsuperscript{70} See WAYNE, supra note 5, at 40, 47 (stating that the surface temperature of the sun is 5785 degrees Kelvin and that the Earth's surface temperature is 288 degrees Kelvin); 1 micron = 10,000 nm.

\textsuperscript{71} For a description of the general aspects of transmission of infrared radiation through the atmosphere, see, e.g., WAYNE, supra note 5, at 42. The scientific aspects are discussed in much greater detail in WORKING GROUP TWO, INTERGOVERNMENTAL PANEL OF CLIMATE CHANGE, CLIMATE CHANGE 1995: IMPACTS, ADAPTATION, AND MITIGATION OF CLIMATE CHANGE: SCIENTIFIC-TECHNICAL ANALYSIS (1996) (listing on pages 92-93 fifty different greenhouse gases, most of them in closely related chemical families).
Lovelock a decade earlier. Once this analysis was well in hand, we built a different analytical system to measure methane, the simplest hydrocarbon and the most abundant one in the atmosphere. Hydrocarbon compounds are greenhouse gases because they absorb infrared radiation in the important 5-20 micron wavelength range. A "greenhouse" hydrocarbon, however, is only important for global warming if its average atmospheric concentration is increasing over the decades.

In 1979, we found about one percent more methane in both the northern and southern hemispheres than had been there eighteen months earlier—and now we were also studying global warming.

We take stainless steel canisters evacuated in the home laboratory to remote sites, fill them with air, and then return them to the University of California, Irvine for assay of the trace gas contents. This operation has expanded from about 100 air samples in 1978, to about 10,000 in 1999. These samples are taken all over the world—the north and south poles, the Pacific Islands, polluted cities, and on aircraft flying up to 40,000 feet. Our initial purpose in collecting these air samples was to measure the concentrations of the CFCs and methylchloroform in both northern and southern hemispheres.

Once we had the air samples in the laboratory, however, we expanded our efforts to include measuring the simplest hydrocarbon, methane. During our first comprehensive north-to-south collection in 1978 from Alaska to Tierra del Fuego, we found that the methane concentration was slightly higher in the northern hemisphere than in the southern, about 1.6 ppmv versus 1.5 ppmv. When we made another broad latitudinal collection in 1979, we found that the concentrations had risen slightly in both hemispheres.

72. See generally F. S. Rowland et al., Dichlorodifluoromethane, CCl₂F₂, in the Earth's Atmosphere, 9 GEOPHYSICAL RES. LETTERS 481 (1982) (describing how the collection of ground-level air samples in both the northern and southern hemispheres provided field information about chlorofluorocarbons).

73. By comparing the amount of methylchloroform found in the atmosphere with the amount released to it, its average lifetime can be determined experimentally. The lifetime of other molecules, and in particular of the proposed CFC substitutes, HCFCs (e.g. HCFC-22, CHClF₂) and HFCs (for example, CH₂FCF₃, HFC-134A), can then be evaluated by comparison of the relative rates of reactions corresponding to equation (5) for the various other molecules. In 1981, we estimated the average lifetime for methylchloroform as 6.9±1.8 years. The present estimates are for a lifetime of about five years.

74. See Mayer et al., supra note 2, at 1366.

75. Donald R. Blake et al., Global Increase in Atmospheric Methane Concentrations Between 1978 and 1980, 9 GEOPHYSICAL RES. LETTERS 477, 479
As we continued our study, methane levels continued to increase and, in 1999, the average concentrations are 16 percent higher than in 1978, 1.8 ppmv in the north and 1.7 in the south.\textsuperscript{76} Carbon dioxide is an industrial product, originating largely from the combustion of coal, oil, and gas. Methane is also an industrial product, but it arises mostly from biological processes in the agricultural industry. An average cow can give off about half a pound of methane per day. With 1.3 billion cows in the world, the combined emissions become significant on a world scale. In addition to cattle, another important agricultural source is the growing of rice. Methane enters the atmosphere after seeping up through the stems of rice plants during the flooded-field phase.\textsuperscript{77}

During these investigations, we found that pollution can travel many thousands of miles in recognizable form because plumes of air can move long distances without much dispersion into adjacent air masses. We have collected air samples on board large aircraft by pumping external air through a pipe protruding through a metal windowplate into canisters stored within. With this airplane, we have explored the Arctic winter, the burning agricultural waste in Namibia, Zambia, and Brazil, and the air pollution coming off the Asiatic mainland. During 1996 and again in 1999, we collected air with the NASA DC-8 on flights in the tropical South Pacific. On many occasions, remote-sensing instruments operated by another research group on the DC-8 indicated the presence of high concentrations of ozone below our flight level. When we actually descended to the same altitude and into these ozone-rich plumes, we established the presence of considerably higher concentrations of hydrocarbons and nitrogen oxides than those found in nearby air not enriched in ozone. These are the same precursors to ozone formation as those found in urban environments, that is, in local smog episodes, discussed in Part III, infra. Ozone in the

\textsuperscript{76} I. Simpson et al., Recent Changes in the Growth Rate of Methane, \textit{Geophysical Res. Letters} (in press).

\textsuperscript{77} Methane is released to the atmosphere in association with other fossil fuels, from leakage at all stages in the transmission of natural gas from source to use, from termite mounds, from cows and other ruminants, from rice fields, as "swamp gas", etc. Because of this multiplicity of sources widely distributed around the world, an accurate estimate of the release from each of the various sources is very difficult. There is less uncertainty about the sum of all of these releases because measurements of the actual globally-averaged atmospheric concentration of methane can be carried out with considerable precision.
lower atmosphere, as with carbon dioxide and methane, acts as a greenhouse gas by absorbing outgoing infrared radiation; thus our measurements now gave data on three of the important greenhouse gases: methane, CFCs as a class, and tropospheric ozone. The plumes, we discovered, did in fact originate at the surface. Because the commercial aircraft industry needs information about the wind directions at all altitudes on a global basis, balloons are sent up all over the world every six hours and their motions are tracked by radar. The global civil aviation authorities do not discard the wind direction and velocity records after their short-term predictive utility for air traffic has expired, but instead they store the records permanently. Many months later, we are able to call back this information to make calculations reversing these known wind patterns from the location at which our plane passed through an ozone plume along the path followed by this plume during the two weeks prior to our encounter. For example, in 1996, we went through an ozone plume near the island of Fiji whose winds could be traced back across Australia, then the Indian Ocean, and then into southern Africa. Such plumes usually originate from the combustion of agricultural waste or clearing of forests, commonly described as “biomass burning.” From previous experience with biomass burning plumes in Brazil and southern Africa, we have a catalog of many hydrocarbons known to be formed by the combustion of cellulose-based plants. These hydrocarbons have average lifetimes ranging from a few hours to several weeks or months. The presence of excesses of the longer-lived, but not the shorter-lived gases, indicated a travel time of a week or more and, therefore, a plume originating in Africa, many thousands of miles away.

B. Increasing CO₂ Concentrations are Linked with Increasing Global Temperature

The primary concern associated with the accumulation in the atmosphere of additional carbon dioxide and methane and other “greenhouse gases” is their potential for warming the

78. Nicola J. Blake et al., Influence of Southern Hemispheric Biomass Burning on Midtropospheric Distributions of Nonmethane Hydrocarbons and Selected Halocarbons over the Remote South Pacific, 104 J. GEOPHYSICAL RES. 16,213 (1999). Trajectory calculations have demonstrated that high pollution levels of carbon monoxide found in Tennessee and other locations in the eastern United States have originated in forest fires in the Canadian Northwest Territories 2,000 miles away. See Gerhard Wotawa & Michael Trainer, The Influences of Canadian Forest Fires on Pollutant Concentrations in the United States, 288 SCI. 324 (2000).
planet and changing the global climate. During the last million years, the Earth has passed through a series of very cold spells (the Ice Ages) interspersed with warmer, interglacial periods, such as the current one which began about 10,000 years ago. The glaciers, which have accumulated in Greenland and Antarctica (and the sediments at the ocean bottom), contain within them sequential geophysical records of these atmospheric and oceanic changes. In the Peruvian Andes, the seasonal cycling between moisture-laden winds from the Amazon basin and dusty winds from the Chilean Atacama Desert provide alternating layers of glacial ice and dust that identify the passage of the seasons. In other situations, the detailed composition of the water molecules in the ice itself, the isotopic ratio of deuterium to hydrogen, or of oxygen isotopes of masses eighteen and sixteen, respond to the ambient temperature at the time the water vapor molecules condensed to droplets. The ice cores preserve these isotopic signatures of winter and summer, again permitting the counting of annual layers. On time scales running to hundreds and thousands of years, the isotopic signatures also record the ebb and flow of temperature changes during the alternating ice ages and interglacial periods.

The cores are not pure ice, however, but contain trapped impurities, such as the Quelccaya glacier dust, and gas bubbles no longer in contact with this year's air. The Vostok station in Antarctica, built by the Soviets and now operated by the Russians, is located at 11,500 feet altitude, 830 miles from the south pole. It has an average year-round temperature of about -67 °F and once reached a record low of -129 °F. Such cold air can carry very little moisture and the glacier ice accumulates at Vostok at a rate of only about one-third inch per year. Ice cores have been drilled down to a depth of 3,600 meters, back to layers laid down 420,000 years ago. These cores trap air as they accumulate. About ten percent of the ice volume is trapped air and analysis of the composition of these bubbles provides information about the composition of the atmosphere over these past 420 millennia. The concentration of carbon dioxide in these gas bubbles varies in close correlation with the isotopic temperature scale—the low values are about 180 ppmv in the coldest part of each ice age, rising to 280 ppmv in the

79. This layering is quite visible in photographs of the Quelccaya glacier taken from the side.
80. See J. R. Petit et al., Climate and Atmospheric History of the Past 420,000 Years from the Vostok Ice Core, Antarctica, 399 Nature 429 (2000).
interglacials. The atmospheric carbon dioxide concentration held steady around 280 ppmv for the last 10,000 years until about the beginning of the nineteenth century. Since that time, the concentrations have risen steadily to the present levels of about 368 ppmv, coinciding approximately with the industrialization of the planet and the world's increasing dependence on carbonaceous fuels. Similarly, methane concentrations cycled between 0.35 ppmv in the coldest times and 0.70 ppmv in the warmest periods up to the early 1800s, when the rise toward the current 1.78 ppmv began.

C. Atmospheric Modeling, Satellites, and Recent Temperature Records Confirm Global Temperature Increase

The Earth absorbs energy from the sun, mostly in the visible and near-infrared wavelengths, and emits an equivalent amount of energy in the far infrared. A straightforward calculation can be made of the amount of solar energy absorbed by the Earth from its distance from the sun (93,000,000 miles), and its average reflectivity, or albedo of 30%. The average Earth temperature required to emit an equivalent amount of infrared energy is then another simple calculation, if all of this infrared energy escapes to space. This calculation for Earth gives the obviously incorrect average temperature of 0°F versus the actual average temperature of about 57°F. In contrast, the corresponding calculation for Mars works quite well, with good agreement between the calculated and observed temperatures of about -67°F. The explanation for success with Mars and failure with Earth is that essentially all of the infrared emissions escape through the Martian atmosphere, while the greenhouse gases in Earth's atmosphere intercept a significant fraction of the infrared emissions from the surface. The question for Earth is not whether a greenhouse effect exists—the 57°F excess of observed surface temperature over the calculated temperature is the natural greenhouse effect. This effect certainly exists, and it did so in 1800 before the industrial revolution and for countless previous millennia.

The planet Venus with an atmosphere containing 95% carbon dioxide, and a mass about 93 times as large as our

81. See also D. M. Etheridge et al., Natural and Anthropogenic Changes in Atmospheric CO₂ Over the Last Thousand Years from Air in Antarctic Ice and Firn, 101 J. GEOPHYSICS RES. 4115 (1996) (measuring changing concentrations of CO₂ in the ice core over time).

82. See J. R. Petit et al., supra note 80, at 433.
atmosphere, is about 700 °F warmer than calculated by the simple formula above. The Martian atmosphere, in contrast, has only 0.7% the thickness of Earth's atmosphere, which explains why essentially all of the Martian infrared emissions escapes directly to space. The thick Venusian atmosphere absorbs all of the infrared emissions from the surface, and the energy which finally escapes from Venus is emitted from high up in the atmosphere at temperatures much lower than the fiercely hot surface.

On Earth, the various greenhouse gases absorb a fraction of terrestrial emissions, and re-emit them in all directions, including back toward Earth. Because of the effective blockage of some infrared wavelengths, the maintenance of an equilibrium between the incoming solar and outgoing terrestrial radiation requires that more energy must emerge through the windows of transparency. In turn, this requires that the Earth be warmer. The 57 °F temperature increment causes the intensity of the energy emission per square foot of surface to increase by about sixty percent.

Atmospheric model calculations can fit the pre-industrial Earth surface temperatures, including the rather rigorous test that the model must be able to reproduce the very large temperature changes between winter and summer. When these same models are then given the observed increases in greenhouse gases and extrapolated to the year 2100, the calculated surface temperatures rise, depending upon specific assumptions in the models, to the range from 59 °F to 63 °F, an increase over the natural background of 2 °F to 6 °F.83 This jump is the enhanced greenhouse effect associated with the increasing atmospheric concentrations of trace gases. This enhancement, its magnitude, and its climatic consequences are really the primary subjects of current discussions of global warming and the greenhouse effect.

The infrared spectra of the important atmospheric trace gases are all very well known from laboratory research, and Earth-pointing infrared detectors on orbiting satellites directly confirm that much less radiation is escaping to space in the specific wavelengths absorbed by carbon dioxide, methane, nitrous oxide, and other greenhouse gases. In the transparent

83. See IPCC, supra note 65, at 289 (providing temperatures converted from Celsius). These numbers, however, have been revised upward to a range from 2.5 to 10.4 degrees Fahrenheit in the final working draft of the next IPCC report, according to Andrew Revkin, writing in The New York Times on October 26, 2000. This IPCC report is scheduled to come out in 2001.
regions not obscured by these atmospheric gases, the same
satellites also record the expected large variation in infrared
intensities while viewing surfaces with temperatures varying
from Saharan desert sands (117 °F) to the high Antarctic plateau
(-40 °F).84

Widespread precision measurements of temperature have
depended first upon the invention of the thermometer and then,
for global coverage, on its deployment in great numbers around
the world. A sufficiently broad distribution of thermometers,
many of them on merchant ships, permitting an estimate of
global average temperatures was not reached until the last
quarter of the nineteenth century. Thus, we now have
approximately 120 years of a good global thermometric record.
This record shows a temperature increase of about 1.1 °F during
that period. All ten years of the 1990s, even those cooled by the
volcanic eruption of Mt. Pinatubo, are included among the
warmest fifteen years in the entire record.85

Unfortunately, the public discussion of this global
temperature change has been blurred over most of the past
decade by discussion of a twenty-year data set recorded from a
succession of satellites. The data have been interpreted by some
as showing no significant temperature change over those two
decades.86 The process by which a thermometer registers
temperature through direct exchange of kinetic energy between
its surroundings has long been well understood. In contrast,

84. For a figure illustrating a typical infrared spectrum as observed from a
satellite, see WAYNE, supra note 5, at 42. The spectrum, taken over the tropical
Pacific near midnight, shows clearly: (a) that IR emission goes on both day and night,
and (b) the wavelength patchiness of terrestrial emissions because of the absorptions
by carbon dioxide, ozone, and other gases.
85. See R. G. Quayle et al., An Operational Near Real Time Global Temperature
Index, 26 GEOPHYSICAL RES. LETTERS 333 (1999); J. Hansen et al., GISS Analysis of
Surface Temperature Change, 104 J. GEOPHYSICS RES. 30997, 31015 (1999). See
generally P. D. Jones et al., Surface Air Temperature and its Changes over the Past
150 Years, 37 REV. GEOPHYSICS 173 (1999) (reviewing surface air temperature records
of the past 150 years).
86. See, e.g., DIXY LEE RAY, supra note 35, at 18 (1993) (asserting that "[f]inally,
perhaps the most accurate and most comprehensive recorded temperatures come
from space-based instruments orbiting the Earth since 1978. Tiros II, a temperature
measuring satellite has orbited from pole to pole, over oceans and land, making
continuous temperature records 24 hours a day. These voluminous data show no
significant temperature trend, either up or down."); RONALD BAILEY, ECO-SCAM: THE
FALSE PROPHETS OF ECOLOGICAL APOCALYPSE 147 (1993) (stating that "[s]atellites
orbiting the earth for the last thirteen years that detect atmospheric temperature
differences as small as 0.01 C degrees [0.018 degrees Fahrenheit] confirm that there
has been only a statistically insignificant upward trend of 0.06 C degrees in global
atmospheric temperature during the 1980s.").
sensing from a satellite 500 miles above must depend upon some form of radiation transmitted through space. Molecules of oxygen do give off amounts of radiation that are temperature dependent and these fluctuations can be recorded by satellite. Most of such molecules, however, are not present in Earth's surface. Rather, they are located in the atmosphere at various altitudes between the satellite and the surface. The resulting signal is a summation over sources of different strengths at various altitudes. In November 1999, a committee of the National Research Council, which included specialists in both ground-based and satellite types of measurement, concluded that the ground-based temperature information was correct.87

Atmospheric modeling requires knowledge not only of changes in the trace gas composition of the atmosphere, but also involves understanding the behavior of clouds, of material and energy transfer between atmospheric gases and the oceans, and the presence of atmospheric particles or "aerosols." The largest volcanic eruptions, such as the Philippine Mt. Pinatubo in June 1991 and the Mexican El Chichon in April 1982, are known to put sulfur dioxide directly into the stratosphere where it is chemically converted into particles of sulfuric acid. This sulfuric acid layer reflects some of the incoming solar radiation back into space, causing a predictable lowering of the global atmospheric temperatures for about two years until the particles have dropped out of the stratosphere and washed completely out of the atmosphere. A related effect exists from the burning of high sulfur coal, but these compounds remain in the troposphere where the particles are more transitory. The cooling effects from these particles are concentrated largely in the regions downwind of the sources—transnational pollution occurs regularly in Western Europe and the eastern seaboard of the United States is affected by the high-sulfur coal burned in the Midwest.

Modeling of the atmosphere that includes these various considerations now reproduces satisfactorily, but not perfectly, the observed global temperature record. The Intergovernmental Panel on Climate Change (IPCC) concluded in 1995 that "the balance of evidence suggests a discernible human influence on climate."88 This statement embodied not only the conviction that the global temperature was increasing, but also the conclusion

87. See generally Panel on Reconciling Temperature Observations, Nat'l Resource Council, Reconciling Observations of Global Temperature Change (2000) (the primary authors of the articles reporting the satellite data were both on the committee which produced this report).
88. IPCC, supra note 65, at 4.
that human activities were playing an important causative role. The most significant of these actions are those that release carbon dioxide to the atmosphere, and these are dominated by the production of industrial energy to power the existing demands of our global society. The world's primary industrial energy production in 1998 amounted to 440 exajoules, where one exajoule equals $10^{18}$ joules. The global percentage distribution of energy among the various sources for the year 1998 is oil (35 percent), coal (23 percent), natural gas (20 percent), nuclear (6 percent), hydroelectric (2 percent), and biomass fuels, including fuelwood, charcoal, crop wastes, dung, and biomass-derived alcohol (13 percent). Geothermal, wind, and solar and all other renewable sources other than biomass and hydroelectric together accounted for less than 0.5 percent. Ex9

Except for the renewables, all of these energy sources depend upon the transformation of their carbon content into carbon dioxide. It seems to me that energy needs are so pervasive throughout our modern society, and the world's energy supply is so firmly carbon-based, that all attempts to limit the growth of atmospheric concentrations of carbon dioxide will require a thorough re-examination of almost all aspects of twenty-first century life. Since the IPCC statement five years ago, the measured global temperatures have risen considerably.

The public discussion about global warming has been infused with a sense of uncertainty which does not accurately reflect the actual state of the science. The phenomena connected with global warming are very numerous and widespread and the scientific status of the understanding is quite different from topic to topic. In this way, uncertainty in whether the United States will be hotter and drier fifty years from now can be inflated into the feeling that everything about the future atmosphere and climate is cloaked in doubt. In reaction to this, the well-known climatologist Dr. Jerry Mahlman, long-time Director of the NOAA Geophysical Fluid Dynamics Laboratory in Princeton, New Jersey, has provided his evaluation of some specific aspects of global warming, and he has done so in terms of the probabilities that the current consensus understanding is likely to prove correct. It is virtually certain that the increases in greenhouse gases have been largely the consequence of human activities.

90. J. D. Mahlman, Uncertainties in Projections of Human-Caused Climate Warming, 278 SCI. 1416, 1417 (1997). The NOAA Geophysical Fluid Dynamics Laboratory is one of the premier climate modeling laboratories in the world.
and that the accumulation of carbon dioxide will continue. Furthermore, it is also almost inevitable that the increase in greenhouse gases will cause a global heating effect in the lower part of the atmosphere and a decrease in the temperatures of the stratosphere—both effects are already being observed and are expected to continue. As the oceans warm, the amount of water vapor entering the atmosphere will increase, and will return as a 3.5% increase in precipitation per degree Fahrenheit of warming. Sea level is expected to rise between ten to thirty inches by 2100 because of the warming of the ocean alone, with additional increases occurring when more water returns to the ocean from the melting of land-based glaciers (especially Greenland or the Antarctic). The melting of ice floating in water—the Arctic Ocean is an example—causes no change in sea level.) The increase in precipitation will be especially noticeable in the higher latitudes of the northern hemisphere; this influx of lower density fresh water will tend to slow the northward-flowing warm ocean currents. The regional details of the changing climate are more difficult to predict but might still be very significant.

The basic conclusion is that Earth's climate will change in manners both known and unknown and the rate of such changes will depend strongly upon whether mankind places any effective controls on its emission of greenhouse gases. This objective would not be accomplished by simple compliance with the Kyoto Protocol of 1997, as its regulations would, even if fully adopted by every country, only slow somewhat the rate of increase of greenhouse gases in the atmosphere, falling far short of stopping any increase.

III

SMOG

I will now return briefly to the question of smog. While urban pollution and its smokes and smells have a very long history,
the current concerns about "smog" have arisen over the past five decades, essentially coinciding with the increasing amount of gasoline-powered vehicular traffic. Modern smog has two basic components: (1) gaseous pollutants, of which ozone is the prime concern, and (2) particulate matter that obscures visibility or is small enough to pass through human airways into the lungs. Even with increasing production in cities (and biomass burning), only about 10% of global ozone exists in the troposphere, with the remainder present in the stratosphere.\textsuperscript{95} Measurements near cities in the late nineteenth century consistently showed far less tropospheric ozone than is now found everywhere. In addition, the rate of surface ozone increase is intensifying.\textsuperscript{96}

The formation of ozone depends upon the action of sunlight when coupled with coincident release of: (a) nitrogen oxides, NO and NO\textsubscript{2}, and (b) gaseous carbon compounds other than carbon dioxide.\textsuperscript{97} For example, gasoline contains hydrocarbons such as octane, C\textsubscript{8}H\textsubscript{18}, a small fraction of which leaks unchanged into the atmosphere. Some of the octane molecules are only partially oxidized in use, stopping short of carbon dioxide and water as final products. The imperfect combustion leads to the creation of reactive fragment molecules such as carbon monoxide, ethylene (CH\textsubscript{2}=CH\textsubscript{2}), and acetylene (C\textsubscript{2}H\textsubscript{2}), which initiate the ozone-forming reactions in urban environments. The nitrogen oxides are created by high temperature conversion (for example, in an automobile carburetor) of the ordinary N\textsubscript{2} and O\textsubscript{2} of air into two molecules of nitric oxide, NO. While the special geography of Los Angeles was initially thought to be critical as well, and the bowl-like nature of the mountains around Mexico City does tend to trap city air, smog has now appeared and worsened in hundreds of cities all around the world.

The chemical and solar-driven photochemical reactions that produce ground-level ozone begin immediately within a city, intensify downwind and can continue at a slower formation pace for hundreds or even thousands of miles. The consequence of

\textsuperscript{95} J. Fishman et al., Distribution of Tropospheric Ozone Determined from Satellite Data, 95 J. GEOPHYSICAL RES. 3599 (1990).
\textsuperscript{96} See R. D. Bojkov, Surface Ozone During the Second Half of the Nineteenth Century, 25 J. AM. METEOROLOGICAL SOCY 343, 343 (1986); S. Sandroni et al., Surface Ozone Levels at the End of the Nineteenth Century in South America, 97 J. GEOPHYSICAL RES. 2535, 2535 (1992); Alain Marenco et al., Evidence of a Long-Term Increase in Tropospheric Ozone from Pic du Midi Data Series: Consequences: Positive Radiation Forcing, 99 J. GEOPHYSICAL RES. 16617, 16617 (1994).
\textsuperscript{97} See, e.g., WAYNE, supra note 5, at 246-47 for a description of the chemistry of smog. For a detailed description of some of the special aspects of smog problems in Mexico City, see Blake & Rowland, supra note 2.
this is that the pollution streams from individual cities tend to merge together into general pollution of regions such as the southeastern part of the United States and all of Western Europe. This trend is getting rapidly worse in eastern Asia because of the rapid economic development and accompanying motorization of China and India. The experience in Los Angeles since 1950 demonstrates that environmental controls can reduce the smog formation associated with individual automobiles, and can even reduce the total amount of smog formed despite rapid multiplication in the numbers of vehicles. The experience elsewhere in the United States, Europe, and the developing world, however, indicates that cities almost never adopt the necessary regulations until the smog problem has already become severe.

CONCLUSION

All three of these global atmospheric problems—stratospheric ozone depletion, global warming, and photochemical smog—will affect the world during the twenty-first century. The stratospheric ozone depletion problem has essentially been solved, although not before inflicting on the Earth significant environmental change that will endure for most of the coming century. Global warming and global smog continue to worsen as environmental dangers; whether the international community will be able to act in concert to solve these problems satisfactorily is one of the most pressing problems of the twenty-first century.

