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The Changing Atmosphere in 2004

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Early atmospheric studies

All of us breathe from the atmosphere at all times, and each breath involves taking in air containing about 21% oxygen (O_2) and a much smaller amount of carbon dioxide (CO_2), and then exhaling air from our lungs which now has about 16% oxygen (O_2) and 5% carbon dioxide. Green plants on the other hand take in air through the stomata and convert the carbon dioxide into plant matter while emitting gaseous oxygen. Many other processes also take place with exchange of one gas or another between the atmosphere and lakes, plants, rocks or the oceans. While all of these changes are taking place continuously everywhere, the global sum of these exchange processes is not easy to measure. The problem is made worse by the fact that the atmosphere is omnipresent, and transparent except for the clouds. The determination of its molecular composition depended first upon devising an experimental apparatus from which all of the air could be removed, and then of experimental techniques which could separately identify individual transparent gases introduced into this evacuated space.. By the year 1800 scientists had concluded that the atmosphere consisted mostly of just the two gases nitrogen (N_2) and oxygen (O_2) in the ratio of about 4 parts to 1. The experience of all travellers that it was equally possible to breathe in distant destinations, together with the experiments of a few scientists, confirmed that the atmosphere was very similar everywhere in its main composition, although obviously breathing was harder at higher altitudes in the mountains.

In 1804, two French scientists--Gay-Lussac and Biot--extended the study of the atmosphere to much higher altitudes by taking an evacuated sphere up in a balloon to an altitude of five kilometers (16,000 feet), and then filling it there. After bringing it back to the laboratory, Gay-Lussac found its composition to be the same 4 to 1 ratio found at the surface, although there was considerably less of both gases at the higher altitude.. A few months later, Gay-Lussac, responding to the criticisms of some skeptics, took the balloon up alone, unencumbered by Biot, to seven kilometers (23,000 feet), and analysis of this sample confirmed the ratio of 4 to 1, although with even less of both gases. Our present knowledge two centuries later agrees that the components of the atmosphere mix thoroughly, whether light such as helium or heavy such as CCl_3F, to altitudes far above the 50-kilometer top of the stratosphere.

In 1896, the Swedish scientist Arrhenius, realizing that the burning of wood, coal and oil was releasing carbon dioxide (CO2) to the atmosphere, calculated that a doubling of its 0.03% composition in air would cause a measurable increase (3?C) to the globally-averaged temperature of the Earth. This opened up a discussion which has become very pertinent now a century later under the headings of global warming and abrupt climate change. As the 20th Century progressed, other studies confirmed that the atmosphere is not a simple mixture of N2, O2, CO2, and water vapor (H2O) but contained many additional trace gases. If the sensitivity of measurement extends down to 0.0001% or 10-6, then only 9 kinds of molecules are detectable in the non-urban atmosphere--the four listed above, plus methane (CH4) and four inert gases (argon, helium, neon and krypton). With a sensitivity of detection carried down to 10-8, five more gases are found--carbon monoxide (CO), hydrogen (H2), nitrous oxide (N2O), ozone (O3) and another inert gas, xenon. All of these gases except the inert ones are involved in biological processes. Another characteristic of all fourteen is that they are transparent to visible radiation--which means not only that we cannot see them but also that they are not absorbing any of the visible radiation from the sun. Of course, if they did absorb some green or violet sunlight, the energized molecules would break up quickly, and there soon wouldn't be enough of these molecules left for us to detect.

Much of the interesting chemistry discovered in the past several decades involves additional compounds whose atmospheric concentration never rises above 10-8. The key development then is ever-more sensitive techniques for detecting trace gases, driving the level of successful observation down to 10-12 or even 10-15.

At these levels, hundreds of different compounds are detectible in the atmosphere even in remote locations.

Ozone at Ground Level

One of the first sets of continuing measurements made in the same location was initiated in the 1870's at Montsouris, near Paris, where the ozone concentration in surface air was analyzed for two decades. These concentration ratios were observed to be about 10 parts per billion by volume (ppbv), with little change from season to season or year to year. The absence of any change between winter and summer certainly suggests that the sun was not then involved in forming ozone near the ground. One hundred years later, similar decade-long experiments carried out at Hohenpeissenberg, near Munich, Germany, showed higher concentrations throughout the year, and approximately twice as much (40 ppbv vs. 20 ppbv) in mid-summer versus winter. The summertime peak indicates that now there is a solar-driven mechanism for forming ozone near the surface. Recent photographs of central Munich show a brown gaseous layer just above the surface, signalling the presence of the colored molecule nitrogen dioxide (NO2). This brown color is an identifying marker for high urban ozone concentrations. The difference between the ozone measurements of the late 19th century and those one hundred years later is that we now have many human processes which furnish additional gases to the atmosphere. An especially important example involves hydrocarbons and nitric oxide (NO) emitted in automotive traffic which combine with the aid of sunlight to form additional ozone, an important pollutant in metropolitan smog. These processes in urban environments are becoming more and more prevalent around the globe as the population of the world, and its standard living, increase.

Increasing Atmospheric Carbon Dioxide

Probably the most significant change in the last 30 to 50 years for the development of atmospheric chemistry started with the long sequence of carbon dioxide measurements initiated high on the Hawaiian mountain Mauna Loa in 1958 by C. D. Keeling. He also began collecting carbon dioxide at the South Pole that same year. The detection of changes with time in the amounts of carbon dioxide--or any other gas--in the atmosphere requires a long, well-calibrated series of measurements with a high precision technique. His initial CO2 measurements in March at Mauna Loa showed about 315 parts per million by volume (ppmv) increasing to about 317 ppmv in May, and then dropping gradually back to 312 ppmv in October, only to rise again toward another peak the next May. This seasonal cycle with a high in May and a low point in October continued year after year. These changes are caused by the absorption of atmospheric CO2 for photosynthesis by green plants during the spring and summer growing season, and then its escape into the air from decomposing plant life during the autumn and winter. But the cycle doesn't actually reproduce itself from one year to the next. Rather, each month in the new cycle has slightly higher carbon dioxide concentrations than in the corresponding month the previous year, and the yearly average slowly rises to 325 ppmv in 1970. This long term rising background is caused by the combustion of fossil fuels--coal, oil and natural gas--for energy production. Keeling has continued to make these measurements for another 34 years, as they moved upward to the present average concentration of 380 ppmv.

Increasing Sensitivity of Detection from 10-6 to 10-12

Keeling's experiments represent one avenue of advance. Carbon dioxide had long been known as an important component of the atmosphere. His major contribution was making measurements of high precision with enough frequency and over a long enough period of time first to isolate the photosynthetic cycle, and then to recognize the monotonic increase underlying it. Another avenue of scientific advance lies in the extension of the instrumental detection sensitivity to lower and lower concentrations. The British scientist Jim Lovelock invented the "electron capture detector" which increased the instrumental sensitivity for certain molecules--those such as CCl3F which can "capture" an electron--by a factor of about one million, pushing down well beyond the 10-9 level toward 10-12 (parts per trillion by volume, pptv). Lovelock's measurements established that the nearly inert industrial chemical trichlorofluoromethane (CCl3F--also called CFC, for the chlorofluorocarbon class) was easily detectable in the atmosphere at a concentration of about 50 pptv. Furthermore, Lovelock made measurements on shipboard during a cruise from England to Antarctica which demonstrated that this CFC was present everywhere in both hemispheres. The technological uses for this synthetic molecule were growing rapidly in the early 1970's, and most of these uses involved eventual release to the atmosphere.

Chlorofluorocarbons and Stratospheric Ozone Depletion

This was the point in time that Dr. Mario Molina and I began to consider what would eventually happen to such molecules in the atmosphere. We started initially with three questions one can ask for any compound newly released to the atmosphere: first, does it react with sunlight? The observation of color immediately signals that the molecule has absorbed some visible sunlight because the selective removal of some solar radiation is the process which produces the sensation of color. Molecular chlorine (Cl2) is a green gas, and breaks up in sunlight in about one hour with the release of two individual Cl atoms. The second question is: does it dissolve in water? Another Cl-containing molecule hydrogen chloride (HCl) is transparent, and doesn't absorb visible solar radiation. However, HCl is water soluble and dissolves in rain drops to form hydrochloric acid, which later rains out in a month or two, removing the chlorine atom from the atmosphere. And finally, the third question: is there a chemical in the air with which it can react? One of the most frequent atmospheric reactants is the atmospheric oxidizing agent hydroxyl radical (HO) which is especially effective with hydrocarbon compounds. Another type of chlorine-containing molecule, methyl chloride (CH3Cl) , is also attacked by hydroxyl radical (HO) which pulls a hydrogen atom from it to form a water molecule, destroying the methyl chloride in the process. This chemical reaction takes about one year on the average. But CCl3F and the other CFC molecules are: transparent, insoluble in water, and do not react with any atmospheric oxidizing agents. Without any of these tropospheric removal processes the CFCs can bounce around the atmosphere unchanged for decades.

When Molina and I found that these common removal processes weren't effective, we turned our consideration toward solar radiation other than the visible range to which our eyes respond. We are all comfortable with the visible spectrum displayed by sunlight passing through a prism--red, orange, yellow, green, blue, indigo, violet. Or in a numerical description, radiation with visible wavelengths stretching from the lower energy red light around 700 nanometers (nm, or 10-9 meters) to the higher energy, violet light at 400 nm. The sun also emits invisible light, either less energetic--infrared (IR)-or too energetic--ultraviolet (UV)--outside the 400-700 nm visible range. The invisible IR radiation acts as a form of heat energy, while the UV energy in the 200 nm region is absorbed by molecular oxygen, splitting it into two oxygen atoms. Each of these oxygen atoms then reacts with another O2 molecule to form the triatomic molecule, ozone (O3). Most of these processes occur in the stratosphere between 15 and 40 kilometers altitude, forming an ozone layer which then creates the stratosphere. This is a region in which the temperature rises with increasing altitude, and the necessary heat for this warming is provided by the absorption of additional solar UV by the ozone molecules. The ozone molecules are very good absorbers of UV sunlight, especially at wavelengths shorter than 295 nm where they are sufficiently successful in capturing this UV light that none of it penetrates to ground level. All of us humans, and all of the biological species at Earth's surface are protected against UV radiation below 295 nanometers, because this "ozone shield" in the stratosphere has absorbed it all.

The CCl3F molecule, and the other CFCs, are also protected from destruction by this stratospheric ozone because they are transparent to all solar radiation above 220 nm in wavelength. The only place the CFCs can find such radiation is to aimlessly wander high up into the stratosphere at altitudes of 25 to 30 kilometers with 98% of the atmosphere now below them. There they encounter some 210 nm UV radiation, absorb it and break apart with the release of a chlorine atom, e.g. CCl3F ? Cl + CCl2F. This chemistry then quickly multiplies as the Cl atom attacks ozone to form ClO and O2, and the ClO reacts with O atoms to form Cl (and O2) back again. This process is called a chain reaction because the Cl atom is not permanently removed but can repeat the process over and over again--in this case, removing about 100,000 ozone molecules for every Cl atom released! The realization that the technological release to the atmosphere of about one million tons of CFCs per year, would be multiplied by 100,000 from the chain reaction, converted what had been for us an isolated but interesting scientific problem into a major global environmental problem—the depletion of the stratospheric ozone layer by chlorofluorocarbon molecules.

Experimental Confirmation in the Stratosphere

Our conclusion in 1974 that the fate of the CFCs lay in UV photolysis in the stratosphere, and was coupled with prospective severe future losses to Earth's protective ozone layer, were all pen-and-paper estimates made by combining the results from several separately known experimental observations. With a market value of two billion dollars per year for the CFCs alone, and perhaps 50 to 100 times that in their uses, the demand was quick for experimental confirmation of these calculations in the real atmosphere. The necessary experiment was very similar to that carried out by Gay-Lussac 170 years earlier--transport evacuated spherical containers up on a balloon, open them at the desired altitudes in the 20 to 35 kilometer range, and return them to Earth for analysis in the laboratory. Two research groups, each based in Boulder, Colorado, carried out such experiments in 1975. Because the altitude target for the balloon was much higher than Gay-Lussac's 7 kilometers, the balloon was unmanned and was equipped with pressure-triggered devices set to open the spheres at a number of different altitudes. The experimental measurements agreed very well with our calculations made a year earlier, confirming that (1) the CCl3F molecule, even though it is about 5 times as heavy as air, did reach the stratosphere; and (2) the CFC molecules decomposed at the altitudes predicted for the photochemical process.

Long Atmospheric Lifetimes for the CFCs

The next step in confirmation of our calculations required measurements of the amounts of the CFC molecules in the global atmosphere, and this in turn meant obtaining surface level air samples from a variety of latitudes in the northern and southern hemispheres, and returning them to our laboratory for analysis. We started out with collections from the West Indies, the U.S. west coast up to Alaska, and from South America. Later we transferred the southern hemisphere collections to New Zealand and other Pacific islands. Our air sample collections in 1979 showed CCl3F concentrations in both northern and southern hemispheres more than double the amounts found in 1971 by Lovelock. Similar results were found by several other research groups, and this increase in global concentration confirmed that these molecules have very long atmospheric lifetimes. The best current estimates are lifetimes for CCl3F of 45 years and for the companion molecule CCl2F2 about 100 years. After these molecules are released into the atmosphere, its natural cleansing actions require many decades to remove the CFCs.

Increasing Methane Concentrations in the Atmosphere

My research group needed only a small fraction of the air trapped in these canisters for the measurements on the CFCs, so we used some of the remaining air for accurate assays of the amount of methane in the atmosphere. While methane had been suspected as a sometime component of air through much of the 19th Century, its presence in air in remote locations was only established in 1948. In our first methane assays in 1978, we found about 1.6 ppmv in the northern hemisphere and 1.5 ppmv in the southern. Then when we collected another set of canisters during the next year, we found slightly more methane in both hemispheres—another atmospheric gas whose concentrations were increasing! The sources of methane are quite varied and many of them are under the control of mankind such as the emission from rice paddies during the flooded seasons, with the methane actually travelling up through the plant stems rather than as bubbles rising in the water. Cows are another important source. With each cow emitting about 200 grams per day, multiplied by 1.6 billion of them worldwide, the cumulative amount is significant on a global basis. We have continued these global assays for methane every three months since the late 1970's, and have watched the global amount rise from 1.52 ppmv to the present 1,78 ppmv. Any molecule with more than two atoms is complex enough to be a potential greenhouse gas, and over the past century methane has been the second most important after Keeling's carbon dioxide.

The Greenhouse Effect

About half of the solar energy entering into Earth's atmosphere comes in the visible wavelengths with an equal amount in the nearby IR regions and a few percent of the energy arriving as UV light. This incoming energy needs to be matched by an equal amount of outgoing energy or the Earth's temperature would quickly change. (When we talk about the long-term effects of greenhouse gases, temperature changes of perhaps one degree Centigrade over 25 years are mentioned, which corresponds to an increase of about 0.0001°C per day—so the incoming and outgoing energies are almost completely balanced daily.) While the total amounts of energy in and out are closely matched, the wavelength regions for solar emission and terrestrial emission are quite different because these are determined by the surface temperature of the emitting bodies—about 5800 degrees Kelvin for the sun, and 287 degrees K for the Earth—the sun's surface is about 20 times as hot as Earth's. The peak in the incoming solar irradiation lies approximately at 500 nm wavelength (yellow light), while the outgoing terrestrial radiation is around 20 times longer in wavelength, peaking near 10,000 nm, or in the usual terminology, a wavelength of 10 microns, in the “far infrared”.

A very straightforward calculation can be made of the temperature needed for the Earth to emit an amount of energy equivalent to that coming in from the sun, with only two additional bits of data—the distance of the Earth from the Sun and Earth's *albedo*, the fraction (0.30) of solar energy reflected directly back to space, plus the assumption that all of the far infrared radiation emitted by the Earth goes directly into outer space. When this calculation is performed for the planet Mars, the estimated surface temperature is in good agreement with the observed temperatures—almost all of the far infrared radiation does make it into space through the very thin Martian atmosphere. On the other hand, when the parameters for Earth are entered into the equation, the expected temperature comes out as 255 degrees Kelvin (- 18° Celsius), 32°C less than the 287 K (+ 14°C) actually observed. This discrepancy is the *natural greenhouse effect*, which was present in the years 1900 and 1800, and long before that as well.

The modern version of the greenhouse effect discussion is not whether there is a natural greenhouse effect, because there is, and everyone agrees that there is. Rather they are the questions of whether carbon dioxide and methane and other gases added during the 20th Century have already increased the greenhouse effect from 32°C to 33°C, and whether their continued release during the 21st Century will result in a global average temperature of 35°C or perhaps 37°C by the year 2100. An important related point is that the reality of this natural greenhouse effect is not debated—all of the scientific community agrees that the evaluation has been done correctly. And no one has provided an alternative explanation for its cause other than through the greenhouse gas concentrations in the atmosphere.

Greenhouse Gas Absorption

Spectra in the Far Infra-Red The explanation for the natural greenhouse effect is the failure of the assumption that all of the far infrared radiation emitted by Earth escapes to space. It doesn't, and the reason is that the greenhouse gases selectively absorb some of these terrestrial emissions. And Earth has to warm up to produce enough additional far infrared radiation to make up for that absorbed by the greenhouse gases. For each of the greenhouse gases—carbon dioxide, methane, nitrous oxide, CFCs, etc.--there exists a particular pattern in the far IR region of transparent wavelengths and strongly absorbed wavelengths, and the pattern for the atmosphere as a whole is the sum of these individual absorption patterns. The evidence that this absorption actually occurs in Earth's atmosphere is readily obtained with an infrared spectrometer on an orbiting satellite looking down at the Earth beneath. Such satellites record the outward transmission of terrestrial IR radiation in the absorptive and transparent wavelength patterns in the far infrared. When the satellite is over the Sahara desert, the emissions in the transparent far-IR regions correspond to a surface temperature of 47?C, the temperature of the sand below. However, in the major wavelength region absorbed by carbon dioxide, far less radiation makes it into space and the observing satellite because it has been removed by interaction with the carbon dioxide molecules in the atmosphere. An hour later when the satellite is looking down at the high Antarctic plateau, the transparent region detects emissions corresponding to -25?C or colder, while the carbon dioxide absorption region registers even less radiation than expected for this much lower temperature. Clearly, these satellites confirm the reality of the absorption of terrestrial infrared emissions, the basis of the greenhouse effect.

Positive Feedbacks in Global Warming

Once the Earth begins to warm from increased IR absorption by increased greenhouse gas concentrations, there are some positive feedbacks which tend to amplify the warming. In the Arctic Ocean, interfaces exist in which liquid water and floating ice are in contact. As warming occurs, some of the surface ice melts and becomes liquid water. The reflectivities of ice and water are very different: ice reflects most of the solar radiation which strikes it, while water absorbs most of it. The melting of ice causes a very reflective surface to be replaced by an absorbing one, so that even more heat is retained at the surface, contributing to further warming. The same effect is attained at snow-rock interfaces on the land--snow reflects sunlight, rocks absorb it. When the snow melts, much more heat is retained by the rocks, and additional surface warming occurs.

There are many signs in the North polar region now of disappearing snow and ice, and rising temperatures. The Arctic Ocean especially has large areas with water and ice in direct contact. This feedback is not as strong in the South Polar region because Antarctica is predominantly a continent, land covered with 3 kilometers of ice, and with considerably lower temperatures than the 0?C which marks the coexistence of floating ice and cold water.

The Ice Ages

Early in the 19th Century geologists were puzzled by their observation in the European Alps of very large boulders which seemed totally out of place in their surroundings--totally different composition and appearance, often resembling other geologic sites many kilometers away at higher altitudes. Enough of these strangers were found that they were described as a class of out-of-place objects known as the "erratics". Over the last part of that Century, the scientific world became convinced that these boulders had been entrapped in glaciers which had transported them down the mountains, and then, when the glaciers disappeared during warmer conditions, left them stranded in these Alpine valleys. This was the beginning of the present understanding that thousands of years ago the Earth had a much colder climate--an Ice Age, one of a long series extending back one million years or more. At the coldest part of the most recent Ice Age 21,000 years ago, all of Scandinavia, all of Canada, and large parts of northern Europe plus New England and the Great Lakes region of the United States were covered by ice two to three kilometers deep. With all of that water frozen and piled up on the land, the oceans were about 130 meters shallower than at present--Alaska and Siberia were connected by a broad land bridge, England was not an island, and the Black Sea was an inland lake, among many other altered topographic differences from the present.

Glaciers still exist, especially in Greenland, Antarctica, the Alps, the Canadian Rocky Mountains, and many high altitude tropical locations. At the Quelccaya glacier in the Peruvian Andes, the predominant wind directions have a strong alternation every year between moisture-laden winds from the Amazon, and very dry, dusty ones from the Bolivian *altiplano* and northern Chile. The result as one digs down into the glacial ice is a readily visible yearly alternation between ice and dust layers which allows counting back in time for a thousand years or more. In Greenland and Antarctica, the temperature alternation between summer and winter is preserved in the isotopic composition of the water molecules, with changes in the ratios of both 18O/16O and 2H/1H with the outside temperature variations. Moreover, the initial mixture of snow and ice from a storm has large amounts of air mixed in with the frozen water. Gradually as the years pass and more and more ice accumulates creating strong pressures on the buried layers, much of this air is squeezed out. Eventually, as the ice accumulates to a depth of 50 meters or more, no additional air is driven out, and about ten percent of the ice volume is trapped in ice bubbles no longer connected with one another. Inside these individual bubbles is ancient air, with the molecular composition of by-gone eras.

Atmospheric Composition in Ice Core Bubbles

Measurements in ice cores drilled down out of glaciers from regions with very heavy snowfall have concentrations of greenhouse gases such as carbon dioxide, methane and nitrous oxide which show that each of these gases had nearly a constant composition for the last ten thousand years. This period ended only relatively recently, about two hundred years ago, when all three of them began to increase in concentration, as demonstrated by analysis of the more recently trapped bubbles. The carbon dioxide concentrations in these ice cores were about 280 ppmv until around 1800 when a slow rise began, reaching, as we know from Keeling's data, 315 ppmv in 1958 and 380 ppmv now. The increase in carbon dioxide concentration in the atmosphere, of course, corresponds to the exponential expansion in the burning of coal and oil for energy since the Industrial Revolution. The methane concentrations in the air bubbles were about 700 ppbv prior to the years 1750-1800 and then began to rise rapidly toward the present 1780 ppbv. At the highest point of Greenland, known as Summit, and at Vostok, 800 kilometers from the South Pole, ice cores have been drilled several kilometers down, toward air bubbles which were trapped up to 700,000 years ago. During the past 420,000 years, the trapped gases exhibit a series of four ice ages, each separated from the others by an interim warmer period. The air bubbles trapped during the 10,000 years preceding the present 10,000 year period of stable, warm temperatures show very sharp drops in temperature and in the trapped concentrations of carbon dioxide, methane, and nitrous oxide because the period from about 20,000 years ago to 10,000 years ago represented global emergence from the last great Ice Age. Throughout the 400,000 year ebb and flow of the Ice Age temperatures, the amounts of carbon dioxide varied from about 190 ppmv in the coldest periods to 280 ppmv in the warm interglacial periods for more than 400,000 years--until the substantially greater rise in temperatures took over during the last 200 years. In close parallel, methane concentrations varied from about 300 ppbv in the coldest eras and 700 ppbv in the warm periods--until more than doubling during the past 200 years.

We are now living in a period in which the concentrations of greenhouse gases such as carbon dioxide and methane have moved into levels much higher than the Earth has experienced for the past 400 millennia. And the causes of these elevated greenhouse gas concentrations are mostly the consequence of the various activities of mankind.

Smog and Urban Pollution

As is true of many cities, a startling contrast exists between photographs of Santiago, Chile, on clear, unpolluted days and on the much more frequent, visually impaired, smoggy days. Smog comes from two major types of atmospheric pollutant: particulate emissions, and gaseous pollutants, and both of these are often the consequence of automotive traffic. A major gaseous pollutant is ozone formed by the simultaneous presence of unburned hydrocarbons (or carbon monoxide) coupled with nitrogen oxides, with sunlight added to the mix. Our research group has been studying the hydrocarbon precursors to the formation of urban ozone in many cities around the world, including Santiago, Chile. Our standard method relies on the collection of a series of air samples in two-liter stainless steel canisters, transporting them back to the home laboratory, and carrying out analysis of both the qualitative presence and the quantitative amounts of about 200 different chemical compounds. Our ability to detect components at the 10-12 level is sufficiently sensitive that measurable amounts of most of these chemicals are found in the urban atmosphere of almost every city. Typically, we find substantial quantities of hydrocarbons such as methane, propane, butane, hexane, benzene, toluene and nearly 100 others; the well-studied CFCs CCl3F, CCl2F2, and CCl2FCClF2 and many other chlorine and bromine compounds; some sulfur compounds; and lesser-known compounds as well such as the alkyl nitrates (e.g. butyl nitrate, C4H9ONO2). The latter is a marker compound, created as a minor side product from the formation of urban ozone from the molecules butane (C4H10) and nitrogen dioxide (NO2). When we measure butyl nitrate, we know that the butane pollutant has simultaneously formed much larger amounts of ozone through its major reaction path.

In our study of pollution in Santiago, we were aided by 25 students from a local university, who were stationed all over the city in the early morning and filled an air canister at 5 a. m. They then returned to the same locations with other canisters which was filled at 9 a.m. Comparison of the 5 a.m. and 9 a.m. pollution patterns around the city readily distinguished which pollutants were traffic-related, and which were not. Substantial concentration increases were found during this period for carbon monoxide and other compounds long associated with emissions from automotive traffic. On the other hand, propane (C3H8) was identified in approximately equal quantities at both 5 a.m. and 9 a.m., indicating that its presence was not enhanced by the morning rush hour traffic. Rather, both propane and butane are important components of liquefied natural gas, used extensively in Santiago for household heating and cooking, and stored in containers which are often not leak-tight. Such urban measurements can provide information useful for smog-reduction efforts in each city. Mexico City is another city with widespread use of liquefied natural gas, and identification of the importance of its leakage allowed alleviation some of the worst smog contributions by removal of the highly reactive butenes from the composition.

Global Population Growth

While urban pollution has been known for about eight centuries, both the size of cities and the magnitude of their pollution have increased greatly during the 20th Century.

The global population grew from 1.6 billion people in 1900 to 6.1 billion in the year 2000. London was the largest city in the world in 1900 with 4.5 million inhabitants; it doubled in size by 2000, but was now the 20th largest city globally. The contiguous cities Tokyo/Yokohama led the year 2000 list with a population of 29 million people by one estimate, and Cairo was 15th. Only 13 cities were on the 1900 list with populations of one million or more; now there are more than 350 cities over one million, with new additions almost monthly. Most of those cities are also rapidly expanding their automotive traffic, and are suffering from its accompanying smog problems.

Los Angeles ran into serious smog problems in the 1950's and soon began introducing various kinds of regulatory controls. The progress made in cleaning up the air in Los Angeles can be assessed from the official figures for 1965 to the present on the number of days with violations at three progressively worse ozone levels: 95, 200 and 350 parts per billion. In the 1960's Los Angeles violated the 350 ppb standard on 50 or 60 days per year, but the last day with ozone levels higher than 350 ppb occurred in 1982, more than twenty years ago. The last violations of the 200 ppb standard have been one each in 1998 and 2003, down from more than 100 per year in the 1960's. And the number of days in violation of the 95 ppb standard has dropped from about 300 per year in the 1960s to 70 or 80 now. Clearly, regulatory actions can help greatly in reducing urban pollution events, but the Los Angeles situation with regulatory actions which began 50 years ago still leaves much room for improvement with violations of the 95 ppb standard now still found during 20% of the days. There, as in most cities, the impetus for regulation usually doesn't become strong until the local situation is very bad--often from some pollution episode with serious health problems, sometimes including multiple fatalities. In perhaps the most famous example, London's heavy, black fogs were not controlled until after a disastrous several day event in 1952.

Aircraft Experiments and Biomass Burning Many of the chemical reactions involved in urban smog can also be observed in *biomass burning*, the clearing of forests or the burning of agricultural waste. Satellite observations of the Earth after dark show the bright lights of cities every night that clouds do not intervene, and there are a few other regular non-urban light sources such as the flaring of natural gas in the North Sea. The same satellite observations also reveal thousands of lighted areas which last only a week or two, and these are biomass burning locations in Africa, South America, Australia, and elsewhere.

A very important mechanism for investigating the current state of Earth's atmosphere has been the creation of large teams of atmospheric scientists to participate in three-months long, aircraft-based, simultaneous studies of regional conditions all over the world. The overlap both in time and location is a very important aspect because of the large amount of simultaneous background data that becomes available, and is often useful in understanding the whole picture of the particular atmospheric condition being explored. Our research group has been part of fifteen such investigations all over the world since 1988, many of them in the two-decade long NASA-supported GTE (Global Tropospheric Experiment) series. GTE missions in the past decade have often employed two large aircraft, one of them a completely rebuilt DC-8 of commercial origin. Both are configured for our research with a collecting tube extending beyond the fuselage through which outside air can be pumped in to an array of more than one hundred of our usual air canisters.

On one occasion during the 1996 GTE mission in the tropical South Pacific, o the DC-8 took off from Fiji and headed on its way toward its destination in Tahiti. On the initial climb out, the laser instruments operated by another research group on the airplane indicated between altitudes of about 2 to 4 kilometers a plume of air with an unusually high ozone content—at its highest, exceeding the 95 ppb level applicable to Los Angeles. The DC-8 then leveled off at 10 kilometers, and for more than an hour the laser data continued to track the high-ozone plume below. The DC-8 then changed altitude down to one kilometer, a routine pattern change on research flights, passing through the high ozone plume on the way. Our group filled numerous canisters during the descent, and later analysis showed much higher concentrations of numerous hydrocarbons at the plume altitudes than found either above or below. While some such plumes in theory might originate over the ocean or from isolated islands, our experience is that those we have encountered all have origins in biomass burning in distant continental areas.

An entirely separate system of atmospheric experimentation releases radiosondes—balloons equipped to relay back information about their location-- every six hours all over most of the world which are then followed from below to determine from their motions the wind directions and speeds at all flight altitudes. This system is primarily for the use of commercial aircraft in planning their forthcoming flight routes, but the data are not discarded after the route-planning value has passed. Instead these same wind data are stored and can be used months or years later for the calculation of back-trajectories—the path followed by each particular air parcel for the 15 or 20 days prior to its encounter with the aircraft. On this descent, the calculated tracks for the air parcels at altitudes above and below the ozone plume had been over the open Pacific Ocean for more than two weeks. The plume air parcels, however, all tracked back over Australia three or four days earlier, and eventually southern Africa nine to ten days prior to arrival near Fiji. Either Australia or Africa were logical sources for the biomass burning ozone-formation precursors which had created the plume.

Analysis of the composition of all of these canisters disclosed which hydrocarbons and other compounds were elevated in the plume in comparison to those found above and below. Equally important, the chemical analyses also disclosed which compounds were *not* elevated, including some which were well-known to be formed in biomass burning. These compounds were certainly formed, but reacted too rapidly in the atmosphere to survive until their capture by the DC-8 a few days later. For either an African or an Australian burning source, the plume southeast of Fiji indicates that air parcels carrying pollution can travel many thousands of miles with relatively little dispersal. Our analysis indicated that this plume was more than a week old, and originated in southern Africa.

Such long distance spread of pollution is also observed in the northern hemisphere. With prevailing west-to-east winds, regional pollution from the eastern U.S. can reach Europe, European pollution carries to Asia, Asian pollution can cross the Pacific to North America. In effect, the north temperate zone becomes a merged band of ozone pollution stretching around the world between about 25°N and 55°N latitudes. The consequence is that local pollution is not actually confined to its immediate vicinity but becomes regional and eventually global in its effects.

The Antarctic Ozone Hole

I will return now to the CFC-stratospheric ozone depletion situation which I described earlier. Many countries of the world collectively agreed in the early 1950's to an International Geophysical Year (IGY) later in the decade during which all would conduct a wide variety of year-long geophysical experiments in the same time period, so that data would overlap for comparison purposes. The IGY eventually was conducted over an 18-month period from July 1957 through December 1958. The additional six months allowed for year-long studies even in the polar regions where favorable conditions for logistical access are six months apart in the north and the south. Keeling's measurements of global carbon dioxide in Hawaii and at the South Pole were initiated during the IGY, but fortunately were transformed into permanent installations.

The first experimental stations set up to measure the amount of ozone overhead were established in the 1920's, and the longest record is from Arosa, Switzerland, with near-daily measurements since 1931. During the IGY the British Antarctic Survey (B.A.S.) was established and began ozone measurements at Halley Bay on the Antarctic Coast. Because the standard ozone measuring device depends for normal use on direct observation of solar UV light, the Halley Bay data cover the months from October through March, the sunlit months in Antarctica.

During October 1957, and succeeding Octobers for about 15 additional years, the average recorded ozone at Halley Bay was about 300 Dobson Units (D.U.). One Dobson Unit represents approximately one part in 109 of the molecules in the atmosphere, and 300 D.U. is also approximately the average total ozone for the entire world.

However, in the late 1970's the October ozone average measured over Halley Bay began to decrease, and by 1984 the average had fallen below the 200 D.U. mark—values lower than ever previously observed anywhere in the world. The published B.S.A. report of this decline in 1985 attributed the likely cause to effects from chlorine reactions associated with CFC accumulations in the atmosphere. This severe drop in Antarctic ozone was quickly confirmed by NASA's Total Ozone Monitoring Spectrometer (TOMS) on the Nimbus-7 satellite launched in late 1978. The TOMS instrument provided full global coverage with more than 100,000 measurements of ozone each day in both the northern and southern hemispheres, beginning in November 1978. In early October 1979, the TOMS instrument recorded minimum ozone values of about 250 D.U. over a wide area of Antarctica, falling to 170 D.U. in 1983 and 120 D.U. in 1987. The graphic color display of this Southern Hemisphere ozone data led to the description as the “Antarctic Ozone Hole”, and that term has been used ever since.

After the first public announcement of the Halley Bay data, a ground-based expedition was quickly organized to go to McMurdo, Antarctica, in August 1986, and again in 1987, plus a second expedition in 1987 utilizing the NASA DC-8 aircraft and its very high-altitude ER-2 for flights over Antarctica . The ER-2 carried instruments which separately measured ozone and chlorine oxide (ClO), with the latter viewed as a marker for the importance of atomic chlorine—and chain reactions--in the removal of ozone. On August 23 the first successful ER-2 flight from its base in Punta Arenas, Chile, showed very high concentrations of chlorine oxide as the aircraft flew over Antarctica at the flight altitude of 18 kilometers, but little change in ozone. However, this was late winter, and sunlight was just returning to Antarctica after the long winter darkness. By September 16, the ER-2 flight showed chlorine oxide was again very high, and now about two--thirds of the ozone had disappeared during that three-week interval.

The Montreal Protocol to Control CFC Emissions

The ground-based expedition to McMurdo in 1986 had indicated a chemical explanation for this ozone loss, and the accumulated data from both ground and airborne expeditions in 1987 clearly pointed toward chlorine from the CFCs as the major culprit behind the Ozone Hole. These data also convinced the major nations of the world to support the Montreal Protocol of the United Nations, which in late 1987 called initially for a reduction in CFC production by 50% effective with 1999. In London in 1990 this was raised to a full production ban, and in 1992 in Copenhagen the effective date was moved up to January 1996, which is now more than eight years ago. The less affluent nations, which had always produced and used very small amounts of these compounds, were given a deadline delayed by ten years. Ongoing current measurements in the lower atmosphere confirm that the Montreal Protocol is working very well, with the total organic chlorine content—the precursors for stratospheric ozone depletion--actually decreasing slowly from a maximum in 1994—even faster than required by the Protocol. However, a time delay of 5 to 10 years exists between the tropospheric concentrations and the full effect on reduction of ozone loss in the stratosphere. The many decades long atmospheric lifetimes of the CFCs insure that full recovery of the stratospheric ozone layer will also stretch out toward the end of the 21st century.

Global Warming and Climate Change

I'll now return to some aspects of the greenhouse effect and the climatic changes expected in the future. In the present industrial world, the energy sources are, in order of importance, oil, coal, natural gas, hydro, and nuclear power. About 85% of this energy arises from the combustion of the three carbon-based fossil fuels, and the end product of each is carbon dioxide released to the atmosphere. If we examine the geographical sources of this carbon dioxide over the past half century, roughly one-fourth each came from the United States, the Soviet Union and its successors, the rest of the O.E.C.D. countries, from the developing world, especially China and India. In the year 2000 approximately six billion tons of carbon was released to the atmosphere in the form of 20 billion tons of carbon dioxide. The population of the world in 2000 was also approximately six billion, making the per capita emission about one ton of carbon per person. The largest national emission per capita was from the United States with five tons per person per year. Australia and Canada were close behind with more than four tons per person per year.

France with all of its electricity provided from nuclear energy needed only about two tons/year/person. Countries such as India and Nigeria had emissions of less than 0.2 tons/year/person. The intensity of energy usage is closely related to the affluence of the different societies with the exception of those which chosen to go heavily nuclear, or have access to plentiful hydro power. Clearly, any attempt to control carbon dioxide emissions requires solving the problems associated with future growth and development in all countries because of the close relationships among carbon dioxide emissions, energy use and improved standards of living.

Modeling of the future consequences of continued growth in the concentrations of greenhouse gases leads to estimates of a global temperature increase by the year 2100 from 1.5?C to 5.4?C. As discussed earlier, this increase will not be expected to occur uniformly over the globe, but will probably rise at double this global average temperature rise in the high latitudes of the northern hemisphere, which are already showing many signs of a thawing world. Such temperature changes will then be expressed in other physical and biological effects, often quite regional in nature. For example, the Kenai peninsula in Alaska has already suffered the destruction of about 6,000 square miles of contiguous spruce forest, attributed to warmer winter temperatures which allowed much larger survival of its nemesis, the spruce bark beetle. The beetle was already there, and usually was strongly suppressed by the winter cold. When the typical winter-kill failed, the beetle multiplied and destroyed the forest.

A more global result will involve rising sea levels with two factors to consider. The first is the warming of the oceans, which causes water to expand. The second is the melting of land-locked ice, most of which lies over bedrock in Greenland and Antarctica. The current estimate is as much as one meter sea level rise by the year 2100, which would have very strong effects here in the Nile delta surrounding Alexandria, in Lousiana around New Orleans, and for many low-lying island nations like the Maldives in the Indian Ocean. And high-altitude glaciers are melting all over the tropics—such as the Quelccaya glacier in Peru mentioned earlier—as well as in the temperate mountain zones.

The recent Intergovernmental Panel on Climate Change Panel on Climate Change report issued in 2001 concluded that the global temperature had risen 0.6?C over the last century, with much of this increase coming in the past two decades. Thermometers have been distributed widely enough for valid measurements of global average temperatures only since about 1860, and the ten warmest years in that 140 year record have all been recorded since 1990. In the past, the energy output of the sun has varied somewhat, and may have contributed to the “Little Ice Age” experienced by Europe 200 years ago. However, orbiting satellites have measured the energy output of the sun over the past 25 years and have demonstrated that solar energy variations have not been the cause of the rapid recent global temperature increase.

In summary, the Earth is in a period of rapid increase in global temperature for which by far the most likely explanation is the increasing atmospheric concentrations of greenhouse gases, mostly as the consequence of many activities of mankind. The full climatic consequences of a “business as usual” approach to the accelerating emissions of greenhouse gases cannot be definitively estimated now. At the present time, the chief approach toward regulation of carbon dioxide emissions is through the Kyoto Protocol, which at best would only reduce the global growth rate of those emissions by a few percentage points. For many countries, including the United States, the emission rates of carbon dioxide continue to rise, and any substantial regulatory action toward greenhouse gas emissions lies in the uncertain future.

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