

SPRAY CANS, SMOG AND SOCIETY

By

John Sodeau, Department of Chemistry, University College, Cork.

Introduction

In this lecture I intend to describe some of the ways in which our technological activities can couple with the forces of Nature to disturb the position of quasi-equilibrium that our atmosphere has reached. Tom Lehrer's light-hearted "Pollution" song tells what might happen if perturbations to the balance get out of hand:

*"Just go out for a breath of air and you'll be ready for Medicaire.
The city streets are really quite a thrill, if the hoods don't get you
then the monoxide will."*

In the coming hour I will describe how we know that we have an atmosphere, how it got there, what it consists of, what its functions are, disturbances to its compositional balance by pollution events and finally the paradoxes presented by some of the chemicals released to (and created within) the atmosphere.

We take the existence of an atmosphere for granted: the ancients assumed that the Universe was full of "air", which they thought was an elementary substance. They had no feeling for an atmosphere with a certain physical depth and chemical composition. Our technological progress has been such that we can perform spacewalks and photograph Earth from stations orbiting the planet. From the observations it is clear that a "thin blue line" exists above the surface: the nature and functions of this layer of gas (with some particulate matter dispersed throughout) are the central focus of the next section of the talk.

The Atmosphere

In 1630 a pupil of Galileo named Torricelli realised why miners could not pump water out of mines deeper than 32ft. Do you know the reason? The answer is that the weight of the atmosphere at any given point is equivalent to the weight of a column of water 32ft high.

In fact the atmosphere, which is best described as a fluid, extends upwards to about 100km above the surface of the planet. To appreciate how thin it is, think of the Earth as a blown up balloon...the rubber would be thick enough to contain nearly all the atmosphere. It would, of course, be a blue balloon due to scattering of sunlight by the particles that are present in the layer.

It is a remarkable fluid, for even though it is thin, we are kept both warm and protected from harmful wavelengths of solar radiation by it. Without it we could not breathe naturally. In modern times we have learned how to escape it but, as yet, we still cannot control it, as any weather forecaster knows.

The layer we term the atmosphere (Gk. “atmos”= “vapour” + “sphaira”=”ball”) is, in fact, layered itself due to changing temperature gradients at certain altitudes. The first (cooling) region extends upwards to an altitude of 11-15km and contains about 90% of all the molecules in the atmosphere; it is called the TROPOSPHERE and promotes turbulent mixing because hot gases can rise and cold gases can fall. Temperatures fall to about 220K at the top of the troposphere, which occurs at about the tip of Mount Everest, and then rise to about 270K in the layer we term, the STRATOSPHERE. Due to its reverse temperature gradient, vertical mixing of gases is much less effective in the stratosphere and crossover for pollutants at the meeting point between the troposphere and stratosphere is difficult (but not impossible). The layers are shown in Figure 1.

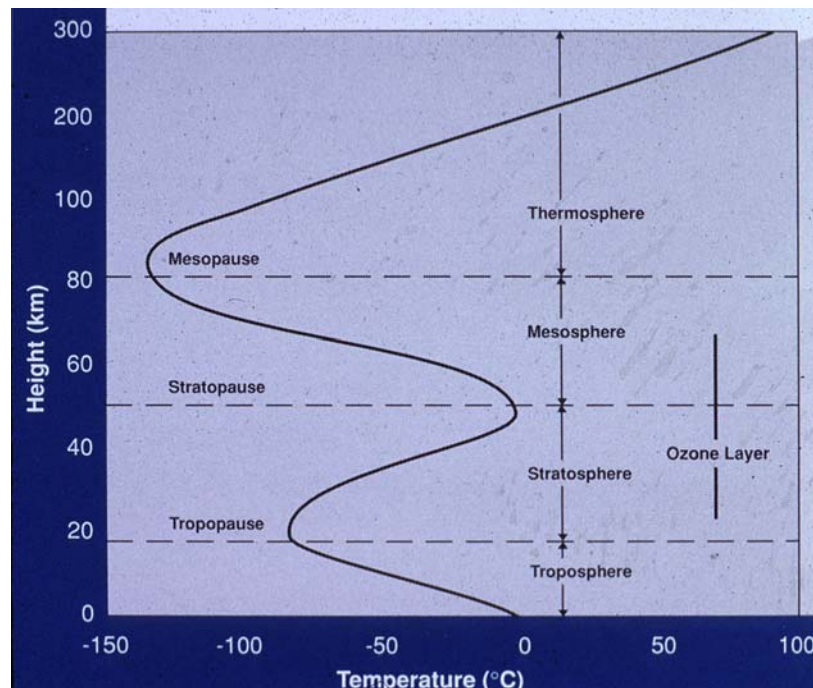


Figure 1. Earth's atmosphere: Temperature profile as a function of altitude

Only certain wavelengths of the solar spectrum penetrate through to the surface of Earth because of the filtering effect that various chemical components of the atmosphere have on the full output. Hence visible light and infrared radiation pass all the way through but higher energy ultraviolet (UV) components do not cross the stratosphere. This phenomenon is fortunate for us because UV light is able to initiate chemistry of a type which is more than sufficient to break the carbon-carbon bonds that are the building blocks of life. In other words our DNA remains relatively unaffected by the Sun's higher energy output thanks to the existence of our atmosphere.

The Sun is therefore a potential destroyer of human life on Earth but, paradoxically, it is also a creator due to its role in photosynthesis. In this process carbon dioxide and water are chemically combined within a leaf, for example, to form carbohydrates and, importantly for us, oxygen gas (O₂). Energetically this process cannot occur simply by thermal initiation but the Sun's visible wavelength output can drive the biochemistry

onwards as long as a “light harvester” is incorporated into the system. Several such molecules do exist in nature and the most important example is called chlorophyll. The subsequent evolution of our atmosphere has taken a radically different turn from that of our neighbouring planets because of photosynthesis. Hence the Earth’s present atmosphere contains large amounts of oxygen and nitrogen gas in a balance maintained by green plants which “breathe-out” O₂ in sunlight, as originally suggested by Joseph Priestley.

In order to confirm that molecular oxygen comprised a real component of our atmosphere, two French scientists, Gay-Lussac and Biot, ascended to 4km during 1804. Their exploration was carried out in a balloon designed by the Montgolfière brothers. They collected samples in evacuated flasks, which were analysed on their return to the surface. The chemical compositions were plotted as a function of altitude and our first aeronomers’ field trips have since acted as a basis for our understanding that air comprises some 21% oxygen and 78% nitrogen.

Actually in modern-day atmospheric chemistry studies it is the compositional breakdown of the final 1% that is the subject of most attention. Hence carbon dioxide at 0.035% and ozone (O₃) at levels ranging from 1-4 x 10⁻⁶ % might appear to be small in relation to the amount of nitrogen gas present in the atmosphere but actually have crucial effects. Even smaller quantities of many molecules and radicals have key importance to the balance of our atmosphere. Their concentrations are so small that their levels are generally quoted as ppm, ppb or ppt values (parts per million, billion trillion). Molecules such as the chlorofluorocarbons and nitrogen oxides exist in the ppb-ppt range depending on altitude as do radicals such as ClO (chlorine monoxide) and OH (hydroxyl). Great leaps forward in analytical methods and monitoring technologies *in situ* have taken place over the last 10 years to make such discoveries possible as will be discussed below.

How do the chemicals, which comprise the final 1%, get into the atmosphere? The two main sources are called BIOGENIC (natural emissions) and ANTHROPOGENIC (“man-made” emissions). Hence nitrogen oxides such as NO and NO₂ are released as a consequence of lightning (which cleaves the strong Nitrogen-Nitrogen bond in N₂ to give a reactive atom capable of combining with molecular oxygen or ozone) or from biomass burning. These chemicals are also released from car exhausts along with hydrocarbons and their partially oxidized offspring. Rice fields and ruminants give rise to methane, ants to formic acid, volcanoes to sulfates, and humans, in the process of breathing out, to carbon dioxide. Nuclear explosions produce radioactive materials; the uncontrolled disposal of refrigerating units produce chlorine-containing compounds; the use of compressed gas sprays for air- or body-freshening release their chemical propellants.

All of the above species can become distributed throughout our atmospheric shield and give rise to major pollution events. Three major examples are described in this lecture: (i) Smogs; (ii) Climate Change; (iii) Ozone “Holes”.

Smogs

4000 Londoners died in a 5-day period in December 1952 due to industrial pollution. The killer was a combination of sulfur dioxide (SO_2) and smoke, which under the near-freezing temperatures and low wind-speeds that prevailed, formed a low-lying, stagnant, humid, foggy layer of trapped, polluted air. Nature had produced an anticyclone; industrial activities had injected acidic particulate matter into the atmosphere and the result was a *smog*, which was a term first coined by Dr HA Des Voeux in 1905 to describe smoke or soot dispersed in fog. The main toxicological danger associated with the sulfur dioxide emission occurs after its oxidation to sulfur trioxide and its conversion to sulfuric acid aerosols and sulfate particles. Indeed the majority of the subsequent deaths were due to bronchial causes as might be expected from inhaling acid deposition of this type and particulate matter capable of penetrating lungs. The correlation is shown in Figure 2.

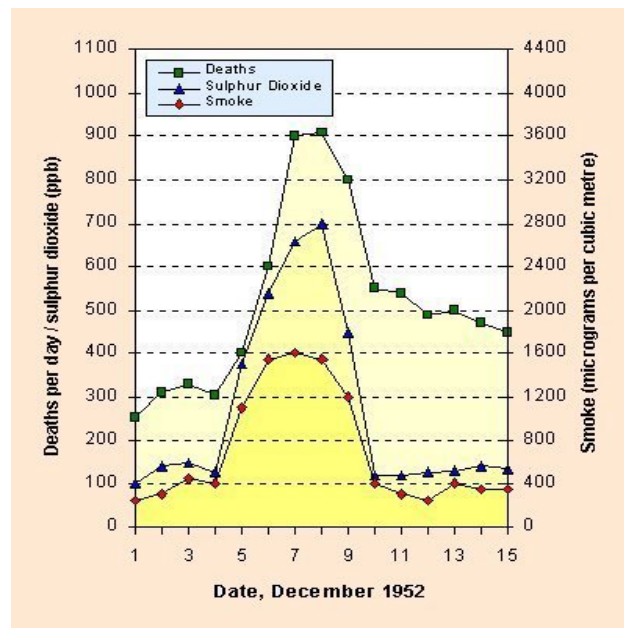


Figure 2. The Great London Smog of 1952: Death rate vs smoke and SO_2 emissions

Losing voters often spurs a Government toward legislation and, in 1956, a Clean Air Act was passed by the British Parliament. It banned emissions of black smoke and decreed that residents of urban areas and operators of factories must convert to smokeless fuels. However as these residents and operators were necessarily given time to convert, fogs continued to be smoky for some time after the Act of 1956 was passed. In 1962, for example, 750 Londoners died as a result of a “fog” but nothing on the scale of the 1952 Great Smog has ever occurred again.

You may be surprised to learn that Southern California is also a natural smog laboratory even today. The chemistry giving rise to these pollution events is quite different from that

encountered in London in the early 1950s but no less damaging to health. Los Angeles can be considered to be a Petri dish inside that laboratory because of its topography, sunshine and car exhausts. In fact its smogs predate the introduction of the US Automobile because as early as the 1700s, Spanish missionaries made reference to a natural haze that blanketed the area.

Why do smogs occur in Los Angeles? The major cause is location, location, location. That is the LA Basin topography, with its Pacific Beach outlook and freeway-intensive communities surrounded on three sides by mountains, often results in lighter warm air sitting on top of heavier, cold air pushed in from the ocean. This stable weather condition is called a temperature inversion and, particularly in the summer when there is no wind, a “saucepan with lid” condition evolves as the ingredients for “smog stew” are produced by the City dwellers. The two main chemical foods added to the pot originate in the petrol engine combustion process and are: (i) nitric oxide (NO), which, when oxidized, produces a brown-coloured, noxious gas called nitrogen dioxide; (ii) hydrocarbons, which are produced both from traffic and, less effectively, from orange groves. (This latter fact, of course, explains the missionaries’ observations of the 1700s).

The cooking analogy breaks down at this point because the source of energy to initiate the chemistry is not heat but light. Solar energy can break down the brown, nitrogen dioxide gas to produce a reactive oxygen atom; the process is particularly efficient in Sunny California. O-atoms can add to molecular oxygen to produce the toxic chemical, ozone or react with the hydrocarbons to make partially oxidized organic compounds, which are reactive with many other chemicals including nitrogen dioxide. The resulting mixture cannot escape upwards or outwards because the prevailing northwesterly winds sweep in from the ocean and press the mixture against the mountains. The overall condition is called a PHOTOCHEMICAL SMOG and is unpleasant as anybody who has visited Disneyland on a bad day can testify.

Climate Change

The forecast of climate change as a consequence of human activities began with a prediction made by the Swedish chemist, Svante Arrhenius, in 1896. In addition to his fundamental works on reaction kinetics, Arrhenius took note of the industrial revolution then getting underway and realized that the amount of carbon dioxide being released into the atmosphere was increasing. Moreover, he believed that carbon dioxide concentrations would continue to increase as the world's consumption of fossil fuels, particularly coal, increased ever more rapidly. His understanding of the role of carbon dioxide in heating Earth, even at that early date, led him to predict that if atmospheric carbon dioxide concentrations doubled, planet Earth would become several degrees warmer. However, little attention was paid to what must have been seen to be a rather far-out prediction that had no apparent consequence for people living at that time.

Arrhenius was referring to a potential modification of what we now call the Greenhouse effect, the “blanket” phenomenon provided by the atmosphere that keeps us warm. The question is: How does it work?

Visible wavelengths of the Sun’s radiation pass through the clear atmosphere relatively unimpeded and are degraded eventually to heat on the surface of the planet. The subsequent infrared (IR) wavelengths emitted by the warm surface of the Earth are absorbed partially and then re-emitted by a number of trace components in the cooler atmosphere above. The most important of these species are water vapor and carbon dioxide gas. Because, on average, the outgoing infrared radiation balances the incoming solar radiation, both the atmosphere and the surface will be warmer than they would be without the greenhouse gases. This so-called natural Greenhouse effect causes the mean temperature of the Earth's surface to be about 33K warmer than it would be if natural greenhouse gases were not present. This factor is a life-saver because the effect creates a climate in which life can thrive and humans can live under relatively benign conditions. (Imagine if the normal temperature of County Cork was -13°C!)

However our increasing demands for energy and associated technological activities, as predicted by Arrhenius, could give rise to real climate change (correctly termed an “enhanced” or “accelerated” Greenhouse effect). Excessive gaseous emissions of good IR absorbers like carbon dioxide, methane, nitrous oxide (N₂O), and chlorofluorocarbons can contribute to the possible raising of the mean temperature of the Earth's surface above that occurring due to the natural Greenhouse effect. The resultant global warming would probably bring other, sometimes deleterious, changes in climate; for example, changes in precipitation, storm patterns, and the level of the oceans. The “tracking” between CO₂ concentration levels (mixing ratio) and surface warming is shown in Figure 3.

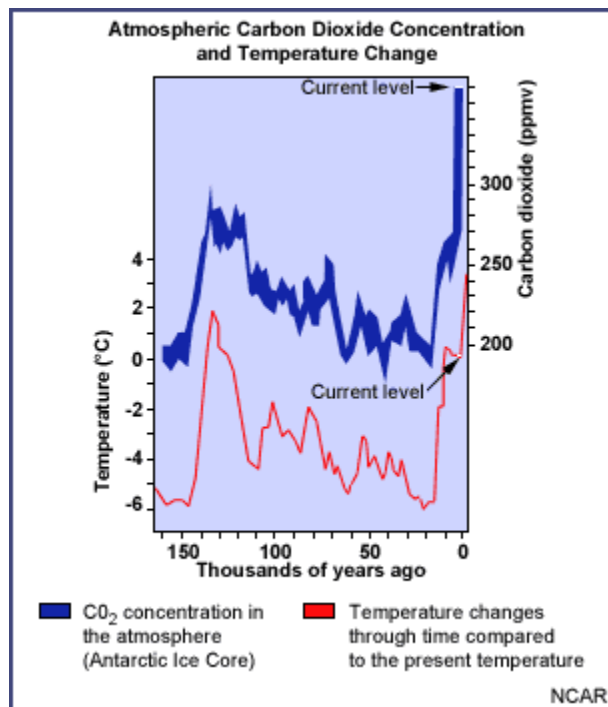


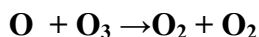
Figure 3. Atmospheric CO₂ mixing ratios and temperature

Ozone “Holes”

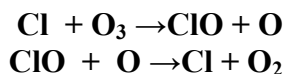
*We will not wait, we go sky high.
Our threatened hate you won't defy!*

W.S. Gilbert's couplet from the operetta, *Iolanthe*, was originally directed to the Peers of the Realm by a few mixed-up Fairies. However the lyrics could equally apply to a song from a spray can containing chlorofluorocarbons (CFCs) to stratospheric ozone. The potential vulnerability of this layer to human technological activities and the serious consequences of “ozone depletion” have been slowly revealed over the last 30 years.

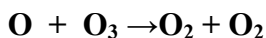
The stratosphere resides between *ca.* 17 and 50km above the Earth's surface sitting on top of the troposphere. It is a relatively dry, stable region although the horizontal mixing of chemical species which reach there is effective over time. Molecular ozone is created by the Sun's photolysis of O₂ to produce reactive oxygen atoms, which can react with their parent to produce O₃. Ozone is an unstable molecule, which is particularly sensitive to light (that is, absorbs the wavelengths) in the UV region 240-310 nm. Over time, a balance between the three oxygen species occurs in the stratosphere to produce a “steady-state” as outlined by Sir Sydney Chapman in the 1930s. The key reaction step in the mechanism is:



The rate at which this ozone-destroying reaction occurs is of central importance to maintaining the “steady-state balance”. In the mid-1970s, two scientists from the University of California at Irvine (F.S Rowland and M.J. Molina) predicted that this rate could be enhanced by a chlorine-catalysed cycle, as follows:



The sum of these two reactions is:



And so the key Chapman destruction step would be accelerated by the addition of chlorine atoms to the stratosphere. Furthermore the chemistry would actually recycle the two reactive halogen species (Cl and ClO) again and again. In fact it has been determined that up to 10⁹ cycles can occur before the Cl atoms and ClO radicals are taken out by other atmospheric species such as methane and nitrogen dioxide. The resulting products, HCl and chlorine nitrate (ClONO₂) are unreactive toward ozone and called RESERVOIR SPECIES.

Notice that the ClO radical is predicted to be formed at the expense of an ozone molecule. At the time when the above catalysed, ozone-destroying chemistry was suggested much scepticism was voiced, particularly from industrial manufacturers of

CFCs. However even in the 1970s it was clear that if a ClO/O₃ anti-correlation was to be observed in actual stratospheric field measurements, then crucial evidence in support of the Rowland-Molina suggestions would have been found.

But even if the theory is correct, what effect would stratospheric ozone depletion have upon us? The answer is to be found in the property of ozone to absorb wavelengths of light between 240 and 310 nm. As mentioned above, UV wavelengths in this region can break down DNA giving rise to both human and ecological damage. Hence, ozone is effectively our planetary sun-tan lotion or light filter and its depletion in the stratosphere would have severe biological consequences for us all.

For the Rowland-Molina theory to reflect reality, of course, chlorine atoms would have to ascend from ground-level or be formed in the stratosphere. The most likely method of the two would be for an inert compound to float upwards in our atmospheric fluid, cross the tropopause (Figure 1) and break down above it, thereby releasing a Cl-atom. Hence the question arises: are such ozone destructive chemicals being emitted from the Earth's surface?

In 1930, Thomas Midgley, the inventor of chlorofluorocarbons and later a vice-president of General Motors, dramatically demonstrated their safety by taking a deep breath of one of his chemicals and then exhaling it to blow out a candle! However it was this property of inertness, so necessary in a domestic refrigerant, that was their stratospheric undoing. It is clear (with hindsight) that highly unreactive and insoluble compounds such as the CFCs could reach 40km or so high chemically unscathed. But here they could be photolysed by the Sun's output (around 170-210nm for the CFCs) to produce chlorine atoms.

All of the chemical pieces were apparently in place for the stratospheric ozone destruction theory to be real. However in the mid-1970s the theory was still just that: ideas based on laboratory experiments and computer modeling studies. What actual confirmatory field measurements had been performed directly in the stratosphere? Could CFCs reach and surmount the tropopause? What evidence for the ClO radical in the atmosphere existed? Most importantly: was there any indication that ozone levels were actually decreasing?

Then in 1985, along came the Antarctic ozone "hole". This important discovery by the British Antarctic Survey showed that in Austral Spring (October) a massive depletion over the southern polar region was apparent. Over many subsequent years similar observations have been recorded and confirmed by satellite measurements called TOMS (Total Ozone Mapping Spectrometry). Corresponding data over the Arctic region every February (again the start of Springtime) have also been published. So clearly there is an indication that ozone levels can decrease in the atmosphere at altitudes of *ca.* 17 km over the Poles.

Was the reason for the observations due to the Rowland-Molina theory? What do you think given Figure 4? It shows the concentration measurements for ozone and the ClO

radical obtained by analytical instruments placed on board the aeroplane, ER-2 for its September 1987 flight within the Antarctic stratosphere.

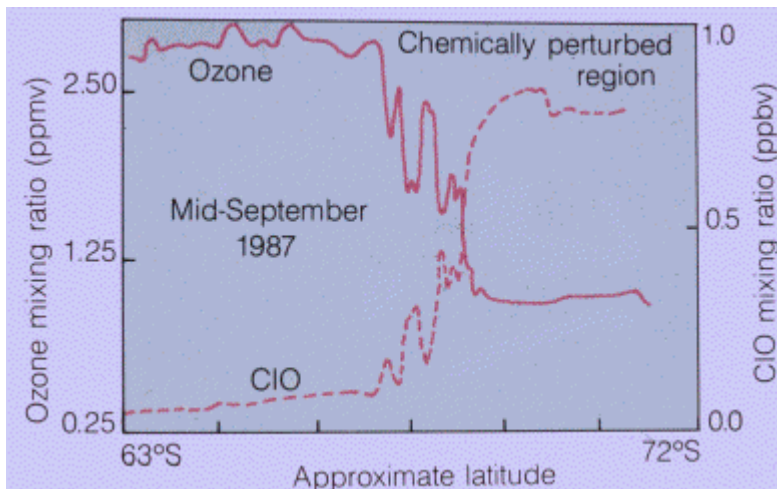


Figure 4. ER-2 measurements taken in 1987, on a sampling trip in the low stratosphere above Antarctica, of the ClO/O₃ anti-correlation.

The clear on-off relationship between the two species provided unassailable proof that at least part of the Rowland-Molina theory was correct: ClO radicals could be formed at the expense of ozone molecules in the stratosphere. But why did the “holes” appear over the Poles in springtime after a period of darkness?

The foundation stone of the explanation is that somehow the balance between the inactive reservoir species (HCl, ClONO₂) and the ozone-destroyer, ClO, is shifted over the Poles during the springtime period. Between 1985-1995 it was shown theoretically and in the laboratory that water-ices could both ionize molecular HCl to chloride ions and break ClONO₂ down to subsequently release ClO radicals. These processes are very slow in the gas-phase but are driven forward by the existence of cold surfaces, which act as cryopumps for the reservoir species and catalysts for their chemical transformation. Water-ices actually do exist 17km high during Antarctic and Arctic winters in the form of Polar Stratospheric Clouds (PSCs). Furthermore a meteorological condition termed, a vortex, occurs at the same time giving rise to a still, dark, cold, atmospheric “reaction vessel” in which chemical processing can take place.

When the sun comes up, the warmth generated breaks the vortex down, the ozone destroyers are released from the winter “reaction vessel” and appropriate wavelengths of solar radiation rapidly drive the chemistry on to produce a “hole”.

The type of surface chemistry, which occurs over the Poles has been subsequently proposed to exist throughout the atmosphere involving materials such as sulfate aerosols and cirrus cloud ices. Only time will tell if their potential effects are real.

Conclusions: Paradoxes and Balances in our Atmosphere

Our atmosphere is like a living-room bean bag, the type of seat that used to be so trendy in the 1980s. Sit on one side and another unpredictable side will squash out. This conclusion should come as no surprise when the number and complexity of the chemicals released to the troposphere, the dynamics of a massive water-air-solid system and the existence of human life have all to be taken into account in order to describe the Earth System.

It is even more complicated if we consider the following atmospheric paradoxes. Ozone is a toxic chemical when present at excessive levels in a smoggy troposphere but is a life-saver in the stratosphere. Carbon dioxide is a key component of photosynthesis but again when present at excessive levels will accelerate climate change. Water, which is necessary for both plant and human life can act as catalyst for ozone destruction when frozen in the stratosphere.

The current chemical balance of our atmosphere is about right but it can only be disturbed by “we, the people”, craving more and more energy and associated technological progress to feed our desires for more and more creature-comforts. Remember: there is always a price to be paid for everything but let it not be our breathable, warming, UV-filtering atmosphere.

(This lecture was delivered at the UCC Science Faculty Public Lecture Series 2002-2003, on November 27, 2002.)