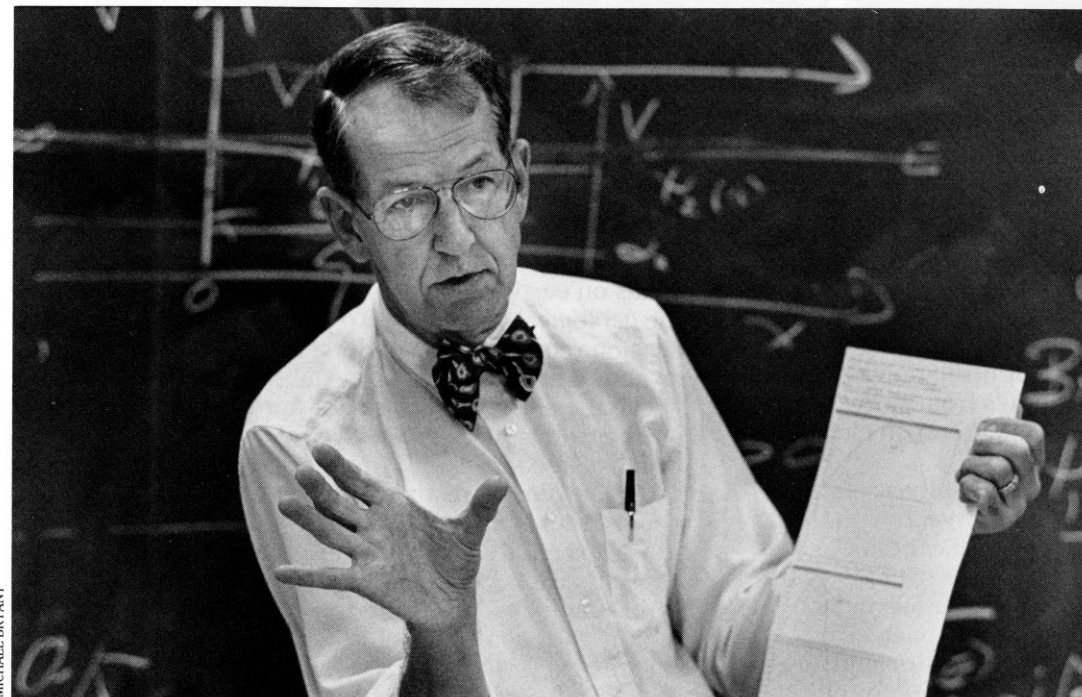


A Global Experiment: CFC's and the Ozone Crisis



MICHAEL BRYANT

by John Chesick
Professor of Chemistry

The ozone layer problem is an excellent case study for students of both the natural and social sciences. Numerous articles on the antarctic (and recently arctic) "ozone holes" document the detrimental effects of activities by the earth's inhabitants. At the same time, we also see the difficulties political systems have in managing serious environmental matters and the consequences that occur long after an elected official's term of office. Our society has turned one-time luxuries into current necessities. We now see societies trying to balance these perceived short-term needs against long-term prices for such necessities.

I became acquainted with the ozone layer problem through the chance reading of an article in 1971. The article estimated the likely effects on the stratospheric ozone layer from exhaust gases produced by a proposed fleet of supersonic jet transport aircraft. My interest in that part of chemistry dealing with rates of chemical reactions drew me to the article, but my knowledge of atmospheric chemistry was nonexistent. After slogging through the text, I concluded that the matter was not only interesting and important but also that the essentials of atmospheric chemistry should be accessible to a general chemistry audience. Some interpretation and rewriting of the materials, however, were necessary for use with such an audience.

This material linked and illustrated a variety of topics in general and physical chemistry courses and resulted in my continuing engagement with the topic in our chemistry curriculum. Ironically, over the last twenty years concern over supersonic jet transport has practically disappeared, but a much more significant source of trouble for the ozone layer has appeared, the "CFC problem," which has *not* gone away with time.

Our story could start in many places, but we can begin it with the advent of practical refrigeration and air conditioning, which shaped where and how we live in ways that we now tend to take for granted. Mechanical refrigeration, ice manufacture and the earliest air conditioning systems employed, until the early 1930s, either liquid ammonia or liquid sulfur dioxide as the essential working fluid. These substances are corrosive, very toxic and combustible. These properties severely limited the design and utilization of refrigeration devices. The ideal working fluid for such equipment should be non-toxic, non-corrosive, non-flammable and reasonably inexpensive to produce and purify. Its task as a refrigerant fluid also requires a conveniently low boiling point. This ideal refrigerant fluid is most simply characterized as *very* chemically inert in our environment.

Around 1930 Thomas Midgley, a chemist working in the Frigidaire division of General Motors, concluded that the chemical requirements severely limited the elements and the types of molecules which could be used. In a neat piece of chemical architectural work, he came up with two simple compounds which contained only the elements chlorine, fluorine, and carbon, namely CFCl_3 and CF_2Cl_2 . This class of compounds, known as chlorofluorocarbons, or CFC's for short, solved the refrigerant problem. They met all the criteria for the next forty years, and were chemically inert in any "reasonable" environment. There were no known biochemical or environmental reasons to be concerned about these materials. DuPont was probably the first major producer of these chemicals designed for use in refrigerators, marketing the materials as "Freons." Refrigerators became safe, common and compact. Central air conditioning made it possible to live in oppressively hot

and humid climates. Automobile air conditioning became standard equipment. Food preservation and distribution patterns changed along with residential and commercial architecture and locations. As often happens as a result of technological innovation, the benign and convenient properties of these CFC's led to the development of other uses such as an essential role in the manufacture of plastic foam for insulation, as propellents in dispensing aerosol sprays from spray cans and as a solvent in removing oil and grease in electronics and other manufacturing.

By 1988 the world-wide production of these substances was over a million tons *per* year, with the United States and the Organization for Economic Cooperation and Development accounting for over 70% of the total. These materials accounted for over 600 million dollars per year of sales for just one company. About 40% of this material was used in refrigeration and air conditioning equipment, and 30% went into production of plastic foams. The dollar value of goods and services involving these materials was, of course, much larger than just the sale price of the CFC's.

This story of technological development and the societal evolution dependent on it eventually connects with a much older story, that of the structure of our oxidizing (oxygen containing) atmosphere and the life forms on earth which evolved in this atmosphere over the geological time scale. To proceed further in the discussion requires some understanding of the layered structure of the atmosphere and some of the functions which these layers perform for our biosphere.

The troposphere is the layer of the atmosphere which is in contact with the surface of the earth and which we most directly experience. Weather—winds, clouds, rain, snow—takes place in this layer. Airplane travel, except that of the highest performance supersonic aircraft, also occurs in this layer of the atmosphere. Atmospheric pressure and temperature both drop rapidly with increasing altitude throughout this region.

The next layer of the atmosphere, the stratosphere, is special for us in two ways. First of all, it contains a small amount of ozone, the triatomic oxygen molecule O₃, which acts as a sunscreen, removing most of the part of the light from the sun that is harmful to us.



One of the islands in the Tampa Bay Sanctuaries

Sanctuary Manager and Biologist: Richard Paul '68



“If we do not take wildlife into account as we contemplate development and other land uses then wildlife will simply disappear,” said Richard Paul '68, manager and biologist at the National Audubon Society's Tampa Bay Sanctuaries. Primarily Paul is the steward of the nearly 15,000 breeding pairs of pelicans, egrets, ibis, bills, herons and cormorants that inhabit the ten small islands, eight natural mangrove keys and two artificial dredge material islands that constitute the Tampa Bay Sanctuaries.

But securing the breeding grounds for these birds only solves part of the problem. “The birds fly twenty miles or more in search of suitable foraging areas, and if those areas are not available or productive when they get there,” Paul said, “then the birds are in just as much trouble as if they were being directly disturbed at the breeding site.” Fortunately, birds that feed chiefly in coastal waters, such as brown pelicans, usually find sufficient nourishment because government regulations protect coastal wetlands.

However, fresh water wetland systems and the bird populations that depend on them, such as the White Ibis and Snowy Egret, have not fared so well. White Ibis, for instance, have declined by at least eighty percent in the last fifty years.

Much of this problem centers on the distinction between public and private lands. Generally speaking, any land below the mean high tide line is public property, and therefore subject to regulation by the state. Land above the line is private. “There is considerable public discussion going on here and across the country about what kinds of government controls we may institute to direct, restrict or otherwise regulate the private use of land,” said Paul. “Too often, wildlife populations are left out of the discussion.”

To keep wildlife and the environments on which it depends in the decision making process, the Audubon Society focuses on educating the communities that surround the sanctuaries. Towards this end,

Paul coordinates wildlife needs with school groups that volunteer their labor for habitat restoration projects. Often a newspaper reporter or TV crew accompanies the group to not only describe the volunteer projects, but to carry the message about the beauty and values of wildlife to the public. Paul also represents biological concerns for wetland-dependent bird populations to local port authority and community land use groups.

In his work Paul often has to counter the negative image wetlands have acquired in this country. “For a long time in the nation, much less in Florida, marshes and swamps were disgusting places to be filled and made useful as quickly as possible. We now understand that these places provide free flood control, water storage and water filtration, and that they are extremely important to wildlife.

“If we were smart enough to recognize that these places hold and store water, and release it gradually into the system, and [consequently]

restrict our own activities within flood plains and wetlands, we would avoid the damage that occurs every time there is some big flood.” He commented that print and television media race to tally property damage statistics, but they do not report the long-term deterioration of the natural system. “It's not something where a sign dramatically appears. It takes an understanding of the process [of deterioration] and a look at it over a period of years before you get a sense of what is going on. It is one of the very silent, very real losses of the planet.”

The National Audubon Society also seeks to advance federal protection of wetlands. “Federal regulations are under significant attack right now by the Bush administration,” Paul explained. “Bush has said that he wanted to be the environmental President, and he has endorsed a goal of no net loss of wetlands in the country. But what he has done is sanction a revised definition of wetlands that would eliminate millions of acres from

the definition, including a significant portion of the everglades.”

Paul estimates that the United States currently loses 300,000 acres of wetlands a year, mostly to agricultural activity which has traditionally been exempted from wetlands restrictions. He fears the loss could be much greater if government proposals for limiting wetlands protection are approved. If this happens, Paul said, “The government will retreat sharply from its recent role in wildlife and wetland protection. In fact, the Environmental Protection Agency's role in wetlands protection would be eliminated altogether. We certainly want to block those proposed changes and we also want to strengthen regulations across the country.... We simply cannot assume that wetlands-dependent species of fish and wildlife can survive if their habitat is lost. This isn't alchemy. This is addition and subtraction.”



ERIC MENCHER

Second, the temperature in the middle of the stratosphere is also higher than that of the troposphere just below it, and as a result it mixes only very slowly with the troposphere below. Thus the period of time required for materials produced in the troposphere to percolate up to the stratosphere is measured in decades. Likewise, substances produced by processes in the stratosphere take decades to come into our troposphere. This is the key to the long time scale of our problem.

Light from the sun is the source of energy which drives our biochemical world, utilized as it is received by plant photosynthesis, or used later by us as energy stored in the relatively high energy forms of coal and petroleum long after the primary photosynthesis events. Although the atmosphere acts as a window in transmitting visible light to the surface of the earth, it acts as a sunscreen in protecting all life from the shorter wavelength light (ultraviolet light and X-rays) which would be destructive to any biological organism. The layers of the atmosphere above the stratosphere, the mesosphere and the ionosphere, are responsible for absorbing solar x-rays and the ultraviolet radiation of shortest wavelengths. This is the chemically most destructive of the solar light coming to the planet. Only the ozone in the stratosphere is able to remove most of the remaining ultraviolet radiation. Residual ultraviolet radiation which finally gets through these atmospheric screens to the surface of the earth has as its most obvi-

ous effects tanning, sunburn, premature aging of the continuously tanned skin and skin cancer. It also doesn't help terrestrial plants and marine photoplankton species, but they don't complain to us, nor do they vote in elections. The amount of this energetic and generally destructive near-ultraviolet radiation which reaches the surface of the earth is a sensitive function of the amount of ozone in the stratospheric layer of the atmosphere. Thus, any reduction in the ozone layer will result in increased ultraviolet radiation at the surface of the earth with its most obvious effect of increasing skin cancer rates.

Let us now pick up again the CFC connection in our story. In about 1968, the sensitivity of methods used to analyze gas mixtures for trace amounts of compounds containing chlorine and fluorine (common to many pesticides), took a great leap forward with the development of the electron capture detector for use with gas chromatography. This advance in laboratory technology was important for pesticide analysis and other laboratory applications, but its use in our story was quite unexpected. The method was perfected by an English scientist, J. E. Lovelock, who discovered in the course of testing his equipment that he could readily detect the CFC's present in the atmosphere, and that they were present at levels of 1 part CFC to ten billion parts of air. More extensive studies revealed that the compounds were generally present at these levels

throughout the troposphere. Quick calculations using such analytical data show that the total CFC content of the troposphere is close to the total amount produced since their advent in the 1930s. The compounds were indeed as inert as laboratory tests had suggested and were mostly still around. There were no significant terrestrial sinks or modes of destruction for these molecules in the troposphere. Every breath of air contains a measurable concentration of them. The chief mode of disappearance from the troposphere was, and still is, a slow diffusion up to the stratosphere. Because of the slowness with which the layers of the troposphere and the stratosphere mix, the load of the CFC's in the troposphere takes many decades of time before a large fraction of it will move up to the stratosphere. The production and usage of the CFC's at the surface of the earth, however, has grown *faster* than material has been lost upwards, and the content of CFC's in the troposphere at the surface of the earth has therefore continually grown with time.

Already in the 1930s chemists had figured out a simple set of chemical reactions which was adequate to explain gross aspects of the formation and structure of the ozone layer in the stratosphere. Later work had shown, however, that this picture of the ozone layer should also include reactions involving small amounts of natural catalysts for the destruction of ozone. An auxiliary finding was that the potential existed for perturbation of the ozone layer by materials from human, that is terrestrial sources. These additions to the more primitive reaction scheme of the 1930s were being discovered and worked out in the 1968-1974 period, partly in response to the questions concerning the environmental effects of the proposed fleet of supersonic jet transports.

In 1974, F. S. Rowland at the University of California at Irvine, made predictions, based on his synthesis of a wide variety of chemical information, that caught public attention. He saw that CFC molecules which were stable when produced and stored in the troposphere, would slowly percolate up to the stratosphere where they would be decomposed by this ultraviolet light. Each molecule would then split to give off a free chlorine atom, which through a chain reaction system destroys ozone and is regenerated. Each chlorine atom was predicted to destroy 100,000 ozone molecules before it was removed from the arena and left the stratosphere. Chlorine atoms produced in the stratosphere by decomposition of CFC's as a consequence have a catalytic effect in ozone destruction. Reduction in the ozone level would occur in future decades as CFC's eventually arrived in quantity from the troposphere below, with the attendant increase in the amount of harmful ultraviolet light reaching the earth and effects on the biosphere.

The natural level of ozone in the stratosphere is the result of the balance between its production by the action of sunlight and its destruction by other processes.

There is not much total ozone present, but its creation and destruction are going on at high speed. A good analogy is that of a leaky bucket which is receiving a flood of water from a tap and which at the same time is losing the water through a leak in the bottom. There is a tremendous flow of water through the bucket, but the water level in the bucket stays steady when the input rate is balanced by the output rate. However, if another leak is opened in the bottom of the bucket, the water level will drop until it stabilizes at a new lower level. If the leak is big enough, very little water will be retained in the bucket. The water level in the bucket is analogous to the ozone level in the stratosphere. The rate of formation of ozone is relatively fixed, but the rate of destruction and hence the final steady ozone level is dependent on the sum total of natural destruction processes and the destruction processes of human origin.

There was little doubt about the effect of a reduction in the ozone level on the amount of ultraviolet radiation received at the surface of the earth. However there was considerable controversy, particularly voiced by the CFC producers, concerning the magnitude of the ozone reduction expected. This estimation depended on quantitative data regarding a large number of chemical reactions and extensive computer simulations that linked the chemical reaction system with an even more complex computational problem of simulating the three-dimensional mass flows in the atmosphere. But extensive laboratory studies and more refined measurements of species present in the stratosphere by sophisticated rocket and balloon carried instrumentation packages seemed to confirm Rowland's 1974 predictions. Because considerable time is required for the CFC burden in the troposphere to reach the stratosphere, the effects on the ozone layer predicted for the mid 1980s have been small and hard to measure.

The dilemma for politicians and makers of general policy, however, has been that the effects predicted for the *following* decades are large. However, if we wait until then to act, to stop production and usage of the CFC's, it is quite likely that it will take 50 to 100 years for the stratosphere to cleanse itself and return to normal. Thus we have been in the position of running a global experiment. The prediction is that a disaster awaits the biosphere. The cost of believing this prediction is the shutdown or realignment of a major part of our industry and technology of convenience and necessity. If we wait for some years to be certain of the predictions, then we will be stuck with the environmental effects for a century.

In 1976, a panel of the National Academy of Sciences confirmed the essentials of Rowland's theory and projections, and as a result there was a ban in 1977 in the United States and in a few minor producing countries on the non-essential use of CFC's as propellants in aerosol dispensing cans. This accounted for only 30% of the US

production. At the same time industrial research efforts began in the search for an environmentally acceptable substitute for the CFC's. Alternatives to the CFC's in use now should have the same physical properties and be non-toxic, but should be slightly less stable so that they would be degraded naturally in the biosphere. Neither should the alternative contain chlorine or bromine atoms which would cause trouble if the molecules survive to eventually reach the stratosphere.

In 1980, the regulatory climate in Washington changed, and the industrial research to develop alternatives to the CFC's in use stopped. In the five years prior to 1980, DuPont spent over two million dollars *per year* in research and development seeking an environmentally acceptable substitute. In 1980, that expenditure dropped essentially to zero.

After 1980, the scientific evidence and extensive computer simulations seemed to confirm the effects and the long term predictions, but there was no political or commercial movement to act on this information. In 1985, however, the "smoking gun" was uncovered. In that year the British Antarctic Survey announced that the sky had fallen! With the arrival of sunlight in the Antarctic spring of that year half of the polar ozone layer disappeared. Moreover, reexamination of old data

showed that this had already been going on for several years. The situation had become progressively worse, and it was finally recognized in 1985 that the alarming measurements which had been discarded as instrumental artifacts in previous years were in fact correct. In the next three years a heavy program of springtime polar observations verified that this polar ozone loss was not only becoming more serious as the years passed, but also was unambiguously linked to chlorine-containing species coming from stratospheric CFC decomposition. The effects were much worse than had ever been predicted by the most ardent experts.

On a global scale, the refinement of widely collected data has indicated that there has been a real reduction of 2-3% in the ozone layer over the past decade, a significant and serious amount for this time. In response to these findings, Du Pont capitulated, announcing the intent to phase out CFC production, and from 1987 on there has again been a heavy industrial research effort to find acceptable CFC substitutes for the critical usages. The 1987 International Protocol for limitation of CFC production and use, to come into full effect by year 2000, was ratified by most of the producing countries; however, this protocol has been strongly criticized as too little and too late in view of the more recent data.

Discussions of the effects of ozone depletion have tended to center on the known relationship between sun exposure and skin cancer. There are reasonably precise estimates for the rate of induced cancer fatalities caused by each percentage reduction in the ozone layer. This catches the public attention. However, the most globally significant effects are probably those for which there is the least quantitative or even qualitative information. This is centered on the damage caused by ultraviolet radiation to light-sensitive plant systems, with attendant changes in the biosphere and with probable reductions in crop yields. It is clear from computer simulations that changes in the ozone patterns in the stratosphere will also significantly change temperature patterns in that layer. While the effects of these changes on terrestrial climate are hard to predict, some effects are quite likely, and any effects are probably bad news.

It is one of the articles of faith of chemistry that progress is made (or "understanding" is achieved) by reducing complex phenomena to a set of manageable and observable simpler phenomena. It is the goal to isolate and study these simpler steps in the laboratory. Ideally this knowledge of relatively simple reaction steps then serves as a set of building blocks for under-

standing or predicting the behavior of other complex systems. Atmospheric phenomena can be observed in a variety of ways, but direct experiments, as in astronomy, are hard to perform. The predictions of the qualitative and quantitative effects of the accumulated CFC production were based on the combination of a variety of data and involved ultimately complex and demanding computer simulations. These represented a reassembling of results from the tool kit of information concerning elementary physical and chemical processes that had been accumulated by numerous workers over many years. This synthesis represents a general triumph of the enterprise. The surprise evoked by the discovery of the polar ozone depletion reminds us, however, that a simulation is only as complete as the assumptions put into it and that things can be worse than the predictions of the "experts" in environmental issues. There are global experiments running in which we are all participants.

Investigating Incinerators: Cathy Preston Koshland '72



MICHAEL BRYANT

Cathy Koshland, a fine arts major during her Haverford years, now investigates what occurs in the gaps between the pure application of chemistry and the less-than-perfect application of chemical processes in incinerators. In general terms, she uncovers the potential for carcinogenic or toxic substances to form during incineration. Her team at the University of California at Berkeley also is developing a method to detect the release of such substances. Koshland, an assistant professor in the department of biomedical and environmental health sciences, also holds a Ph.D. in mechanical engineering from Stanford University; hence she brings both technical and theoretical knowledge to these issues.

Of most concern, according to Koshland, is the impact of temperature deviations occurring in an incin-

erator. "We look at what happens to those compounds that don't get destroyed directly in flame," she said. If materials hit cooler walls or if they spend a longer time at lower temperatures in the post-flame region, the potential for toxic compounds to form inside the incinerator increases.

To date she has studied three chlorinated compounds. In many instances the parent and any resultant by-product compound are effectively destroyed at temperatures typical of the post-flame region. "But we've also found other compounds [where] under similar conditions you may completely destroy the parent compound and make some interesting by-products." She adds, "By 'interesting,' I usually mean by-products that are actually more toxic than the parent compound. The practical implication is that we could effectively

destroy a parent compound, and persistently have high levels of by-products that are more toxic."

Because incinerators currently monitor the destruction and removal of toxic substances only in terms of the incoming waste, this condition might go undetected. "If they have a recirculation problem—so that instead of a little of the waste or its by-products encountering cooler temperatures, a lot is—but it's still not enough to trigger [an alarm]—you could release it. That is the kind of situation that is of concern to people." In theory, the material released from the combustor will travel through a series of filters and scrubbers which should reduce the amount of toxic substances so that when the incinerator stack releases and disperses the compounds over the countryside, they no longer threaten the environment.

Unfortunately, current technology cannot instantaneously monitor incinerator emissions for toxic chemicals. Koshland said current analytic techniques can identify almost every compound in the emissions, but the analysis time is long compared to the response time desired for control. "By the time you have determined that you have a problem you may have released more emissions of certain compounds than permitted for the year. You need to have a real time monitor." Koshland and her co-workers are developing a technique that uses lasers for rapid detection of chlorinated compounds. Lasers are used to split chlorinated hydrocarbons into fragments and then again to energize the fragments. Certain fragments fluoresce as they release energy. The fluorescence can be rapidly detected and the fragments identified. By using

a fragment characteristic of chlorinated hydrocarbons, they hope to develop an instantaneous system for detecting chlorinated compounds in emissions.

The conditions Koshland studies deviate from normal operating procedures but they represent a potential for emission control failure. Regulatory agencies, according to Koshland, understand the larger picture—the destruction of compounds, and their resultant products. In circumstances when undesirable by-products are formed, the regulatory community still lacks the information and technology to reduce the release of these hazardous substances.

by Scott Curlee '89

