Chlorofluorocarbons (CFCs) in the Atmosphere: Two Decades of Science and Controversy

by

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I. Commercial life of CFCs: Birth and Death in a Century ?

Fluorocarbon chemistry was born in the 1890s and commercialized for use in refrigerators in 1928. In 1988, world consumption had grown to over a billion kg, with 5000 businesses at 375,000 locations producing CFC related goods and services worth more than $ 28 billion a year (1). Now in 1990, there is a call for drastic reduction or an outright ban of CFC production and use.

The very properties which make CFCs commercially useful also allow them to persist in the atmosphere where they may adversely alter the global environment. CFCs are: 1) colorless, transparent, and odorless; 2) non-toxic; 3) non-flammable; 4) thermally stable; 5) chemically inert; and 6) have low conductivity.

Current uses of CFCs include (1) commercial and residential refrigeration and air conditioning; (2) automotive air conditioning; (3) expanding agents in plastic and thermal insulating foam manufacture; (4) cleaning agents for precision electronic equipment; (5) fireproofing of sterilizing gas for hospital and industrial use; (6) freezing of food; (7) intermediate for fluoropolymer production; and (8) aerosol propellants (banned in some countries).

II. Chronology of Studies of CFCs in the Atmosphere

1920 First series of column ozone measurements by ground-based UV spectrometer (Dobson instrument).

The 1970s: The First Decade of Controversy

1972 Mixing ratios of CFCs measured in atmosphere and suggested as tracer for urban pollution, James Lovelock

1973 First global measurements of CFC, James Lovelock

1974 Rowland and Molina hypothesized that:

1) Emissions of man-made chlorinated compounds greatly exceed emissions of natural ones.

2) The lifetimes of CFCs are relatively long (40-150 years) and concentrations are expected to steadily increase in the atmosphere. CFCs are finally lost through a breakup by UV radiation in the stratosphere.

3) Chlorine and ozone enter into a catalytic cycle where one Cl fragment can destroy 10,000 to 100,000 ozone molecules before the fragment is removed. (Cl initiator reappears as product and process is repeated). (Removed in rainfall as HCL).

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$
$$ClO + O \rightarrow Cl + O_2 \quad (2)$$

4) The ozone layer is thence depleted and more UV radiation penetrates to earth.

5) Increased UV radiation is harmful to biota, including humans.

1976 U.S. National Academy of Sciences report estimated that at 1973 levels, 2-20 % depletion of ozone would occur in 100 years, with probable value of 6-7.5 %.

1977 New fast reaction of HO_2 + NO increased estimates of depletion to 15% UNEP World Plan of Action on the Ozone Layer. Sweden bans aerosol propellants using CFCs.

1978 U.S. EPA banned the use of CFCs as aerosol propellants

1979 New estimates of 16-18 % depletion; however, no change in ozone levels detected, but uncertainty of 3-5 % in measurement technique. 2-D models show the latitudinal variation of predicted CFC depletion.

The 1980s: The Second Decade of Controversy

1980 Search for tropospheric sinks begins: photolysis during adsorption on grains of Sahara sand, degradations by reactions with atmospheric ions, metals (meteors), freeze-out on Antarctic snow. No significant sinks were found.

1983 Models are refined to include increases in CO_2 and corresponding reductions in upper-stratospheric temperatures, and shifts in temperature dependence of rate constants. New estimates of depletion are about 5 %.

1985 Vienna Convention for the Protection of the Ozone Layer

1986 National Ozone Experiment (NOZE-1) at McMurdo, Antarctica include ground based measurements of ozone column, and vertical profile by instruments carried aloft by helium-filled balloon. Results: in October 75 % in ozone removed between 14 and 20 km, e.g. total ozone reduced by 1/3, also low concentrations of NO_x were measured and thus not an apparent cause of ozone reduction, Cl concentrations increased. Current models did not include a mechanism to explain findings.

1987 Airborne Antarctica Ozone Experiment, Ozone within vortex reduced to 50 % of 1979 value. Locally depletion as great as 95 % between 15 and 20 km. Period of seasonal depletion extended and low ozone measured south of 60 S.

Montreal Protocol on Substances That Deplete the Ozone Layer, 43 nations signed initially, calling for a gradual reduction of certain long-lived CFCs to roughly 80 % of 1986 levels by 1994 and 50 % by 1998. CFCs projected to contribute to 10-15 % of greenhouse gases.

1988 Ozone Trends Panel results show a decrease 2-3 % from 1969-86 and a wintertime decrease of 2-6 %. Models cannot predict wintertime decrease and overall decrease in Northern hemisphere. Models cannot predict how the depth and extent of the hole will change with increasing Cl. Non linear response indicated. Mechanisms which explains the observations must include:

(1) Effects of heterogenous processes in the polar stratospheric clouds. The clouds soak up water vapor, serve as a reservoir for nitrogen oxides, provide sites for conversion of chlorine reservoir species HCL and $ClONO_2$ into molecular chlorine.

(2) Effects of polar vortex, which include reduced mixing between the polar region and midlatitudes, and cold temperatures within the vortex which shift the balance from

inactive to active Cl species.

Current postulates suggest that heterogeneous chemical reactions on the surfaces of the clouds convert hydrochloric acid (HCL) and hypochlorous acid (HOCL) into molecular chlorine, and NOx are sequestered in the clouds as nitric acid. Sunlight of spring releases atomic chlorine triggering CLOx chain reactions with no nitrogen oxides to react with CLOx, and reactions run unhindered for 5 or 6 weeks in early spring, causing ozone depletions of 95 % or more in some layers of the clouds, and 60 % in total ozone over all altitudes.

Criticisms of Montreal Protocol include: Estimated stratospheric Cl was 0.6 ppbv a century ago. No ozone hole was detected during 1965-70 with stratospheric Cl at 2 ppbv, huge hole today with Cl at 3 ppbv; Under protocol total Cl may be allowed to grow to 5 and maybe 8-9 ppbv. Full recovery of ozone layer not projected to occur unless Cl falls below 2 ppbv (not projected to be possible within the next century).

Other complex interactions must be considered. Increasing greenhouse gases result in enhanced cooling of the stratosphere which increases ozone production. Increasing CH_4, for example, tends to remove Cl, and competes for reaction with OH radicals.

1988 Ozone hole not as pronounced in 1987. DuPont announces a phase-out of CFCs by the end of the century. Other major industries follow suit with corporate policies calling for reductions in CFC use and production.

1989 Ozone hole as pronounced as in 1987, with a 50% reduction. 10 % reduction over mid-latitudes during spring and summer; 3-6 % reduction in Northern latitudes during late winter, early spring. Polar vortex doesn't form in arctic due to effects of land masses on circulation.

Problems with CFC alternatives include: materials compatibility, energy efficiency, needs of developing countries, and product lifecycle. HFC and HCFC substitutes will replace about 40 % current CFC uses if deemed acceptable. HCFCs have shorter lifetime, but still deliver Cl to stratosphere.

Helsinki Conference, 80 countries agreed to end production and use of long-lived CFCs by the turn of the century.

1990 London Meeting: 92 Nation Revision to Montreal Protocol calls for CFC reduction 20 % of 1986 levels by 1993, 50 % by 1995, 85 % by 1997 and 100 % by 2000. Also a 70 % phase out of methyl chloroform by 1995 and 100 % 2005 and an 85 % phase out of carbon tetrachloride by 1995 and 100 % 2000. A phase out of hydrochlorofluorocarbons (HCFCs) by 2040 in included. Upon agreement by India and China to the terms of the Protocol, the Development of a fund of $ 240 million to assist developing countries in transition was included.

III. Lessons Learned from CFC Science & Policy Debates

1. How to establish communication linkages between scientists and policy makers.
2. The art of compromise and cooperation in developing global environmental policies. (e.g. special allowances for countries with low per capita consumption rates).
3. The stage is set for policies to address emissions of other greenhouse gases.
4. The birth of global atmospheric environmental chemistry and physics.

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