

VOLUME 3

COMMENTS ON THE
ADVANCE NOTICE OF PROPOSED RULEMAKING

"OZONE - DEPLETING CHLOROFLUOROCARBONS:
PROPOSED PRODUCTION RESTRICTION"

BY THE

ENVIRONMENTAL PROTECTION AGENCY

SUBMITTED BY

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RANKING COMPOUNDS BY POTENTIAL
FOR OZONE DEPLETION

Ranking Compounds by Potential
for Ozone Depletion

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Ranking Compounds by Potential for Ozone Depletion

1. INTRODUCTION

It is the chlorine in CFC molecules which is hypothesized to lead to the catalytic destruction of ozone. Different CFCs potentially contribute different amounts of chlorine to the stratosphere. Therefore, Rand introduced the concept of "permit pounds" in its Draft Report [Rand, 1979] to reflect this difference between the various CFC compounds under assessment. Du Pont commented in its critique of the Rand Draft Report [Du Pont, 1980c] that the ranking concept made sense in that it would allow focusing of regulatory attention on those compounds with the greatest environmental damage potential and would permit better evaluation of the effectiveness of competing policy designs.

However, we also noted [Du Pont, 1980c] that although the Rand system of "permit pounds" was a good first step, it was an oversimplification of the relative potential environmental impact of individual compounds. We offered an alternative approximation which we believed to be more rigorous.

In the ANPR, EPA has retained the concept of relative ranking ("permit pounds") but has incorporated a relative quantitative ranking which we believe is in error. The ANPR references Lawrence Livermore Laboratory (LLL) as the source of its ranking. We have tried unsuccessfully over the past 2 months [Hapka, 1980] to obtain this data from EPA to enable a comparison to our earlier work. Conversations with LLL personnel [Woebbles, 1980] have confirmed our preliminary analysis that EPA's ranking is not correct, and is not based on the Livermore group's best assessment of the problem.

Ranking Compounds by Potential
for Ozone Depletion

We have discussed this analysis with the Livermore group, and agreed on the methods which should be applied. Subsequently, we have updated and improved our analysis using the best available published data. We submit the results herein [see Table 1]. The differences between the Du Pont and EPA ranking are not trivial [See Table 2], having potentially profound implications for the ability of the producers to supply CFCs if the proposed regulations were promulgated.

Ranking Compounds by Potential for Ozone Depletion

2. DU PONT RANKING SCHEME

The relative potential environmental impact of CFCs on ozone is related to both emissions of the respective CFCs and their individual potentials for causing ozone depletion. In developing a ranking of the "relative ozone depletion potential" of the individual CFCs, we have examined the relevant factors and found that one must consider: a) the CFC molecule chlorine content by weight, b) the rapidity of release of chlorine from the CFC molecule in the atmosphere (i.e. atmospheric lifetime), and c) the efficiency of this released chlorine in depleting ozone (primarily determined by the altitude at which chlorine is released). This latter factor had been overlooked in previous assessments by both EPA and Du Pont, but has now been determined to have significant impact on the results.

Determining chlorine content by weight is a straightforward calculation, but the latter two effects are intimately tied to model results, so will require periodic updating as inputs to the models are refined.

The entire problem may be addressed with a model in one of two ways: a) A steady-state model calculation may be made for a given annual release, say one million tons, of a single CFC. Calculated ozone depletion from the model runs for each CFC may then be compared to yield the relative depletion potential of each CFC, b) Alternatively, the annual emissions of a given CFC may be adjusted in a series of calculations to determine how many pounds are necessary to give a particular value of potential ozone depletion, say 5 per cent. The pounds required for different CFCs may then be compared to yield directly the relative depletion potentials.

Random Compounds by Potential for Ozone Depletion

Du Pont has chosen the latter method, whereas the Livermore group [Wuebbles, 1980] has chosen the former. The two methods are roughly equivalent, although the intimate connection between the method and the model employed is likely to lead to slight, but inconsequential differences in the results.

The relationship to models also leads to a slight complication for CFC-22 (and for any other hydrogen-containing CFC which reacts in the troposphere with hydroxyl (OH) radical). This is true because it is likely that the models are currently overestimating OH concentrations in the lower atmosphere, (See Appendix E) and, if so, the models are underestimating the atmospheric lifetime of CFC-22 and, therefore, its chlorine contribution to the stratosphere.

The model-calculated lifetime of CFC-22 is approximately 12 years, whereas most other estimates are in the range of 15-20 years. A calculation of "ozone depletion potential" of CFC-22 based on the current model calculated lifetime of CFC-22 gives a very small depletion potential. We have taken a conservative position and adjusted the lifetime of CFC-22 to 20 years, i.e., we have assumed that more CFC-22 reaches the stratosphere (to release chlorine which potentially may react with ozone) than the models currently calculate. This leads to the value reported in Table 1. It should be emphasized that the reported "relative ozone depletion potential" for CFC-22 is conservatively very large. It is entirely possible that the depletion potential is actually smaller, which would allow even more substitution of CFC-22 for other CFCs under any permit pound-type system.

Random Compounds by Potential
for Ozone Depletion

The critical point regarding CFC-22 is that the depletion potential cited by EPA is greatly overestimated. A correct treatment must account for both lifetime and altitude of chlorine release. We note further that such a treatment actually increases slightly the "relative ozone depletion potential" for CFCs 12, 113, 114, and 115, compared to the EPA values. We believe that the reported factors herein are a better representation of the relative potential threat to the ozone by individual CFCs than previously performed.

Ranking Compounds by Potential
for Ozone Depletion

3. COMPARISON OF DU PONT vs. EPA RELATIVE RANKING SCHEMES

The Du Pont numbers, derived as discussed in the preceding section, are presented below and compared to those advanced by the EPA.

Table 1

Ranking of CFCs by Calculated
Relative Ozone Depletion Potential
(Normalized to CFC-11)

<u>Compound</u>	<u>EPA Ranking (ANPR)</u>	<u>Du Pont Ranking</u>
CFC-11	1.00	1.00
CFC-12	0.79	0.84
CFC-113	0.77	0.82
CFC-114	0.49	0.61
CFC-115	0.20	0.35
CFC-22	0.18	0.03

The next step is to translate these relative rankings into equivalent CFC pounds, based on CFC-11 = 1.0.

Table 2

<u>Compound</u>	<u>EPA Equivalent Pounds</u>	<u>Du Pont Equivalent Pounds</u>
CFC-11	1.00	1.00
CFC-12	1.26	1.19
CFC-113	1.36	1.22
CFC-114	2.04	1.64
CFC-115	5.00	2.86
CFC-22	5.56	34.00

Ranking Compounds by Potential
for Ozone Depletion

Thus, under the EPA numbers, CFC producers would be allowed to manufacture 5.6 pounds of CFC-22 in place of 1.0 pound of CFC-11 with no net increase in potential harm to stratospheric ozone. However, under the Du Pont numbers, CFC producers would be allowed to manufacture 34 pounds of CFC-22 in place of 1.0 pound of CFC-11, over a six-fold increase. This difference is critical because CFC-22 has the potential for use as an alternate to CFC-12 in a number of large volume applications.

X. APPENDIX H

SCOPE OF PROPOSED REGULATIONS

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1. INTRODUCTION

The only justification for regulation of a chemical by EPA is the need to control the production, use or disposal of the chemical in order to reduce risk to human health or the environment (hopefully on a cost/benefit basis) arising from current practices. After a risk is identified, a regulation may be devised to control the risk. The regulation should focus on the source of the risk and it should be demonstrated that the regulation will, indeed, reduce or control the risk -- else why regulate?

Opposite this logic, we find EPA's ANPR proposals for the control of CFCs to be seriously deficient in both logic and justification. In this section we question EPA's justification for 1) proposing to control all CFCs, yet neglecting other compounds of potential concern opposite stratospheric ozone depletion, 2) including all CFCs regardless of lack of technically supportable findings that all CFCs are of significant risk to stratospheric ozone, 3) including in the proposal scope compounds which potentially are part of the solution to CFC depletion of ozone (if it occurs), rather than a significant part of the problem, and 4) not exempting CFC uses which result in no emissions, when the stated concern is over the potential effect of CFC emissions, not the use.

Scope of Proposal

2. JUSTIFICATION FOR PROPOSING TO CONTROL ONLY CFCS?

The Clean Air Act is concerned with potential damage to stratospheric ozone from halocarbons or other sources. The NAS examined CFC-11 and CFC-12 and to a lesser extent other potential sources of ozone depletion. Yet EPA states in the ANPR:

"Potential ozone depleters found outside the CFC chemical family may eventually require regulatory action as well. However, the present set of regulations would be limited to CFCs only because there does not exist sufficient information on other depleters,"...

This statement should be contrasted with the NAS finding that:

"Atmospheric measurements indicate that methyl chloroform is contributing between a quarter and half as many chlorine atoms to the stratosphere as are CFC-11 and CFC-12. If it gains increased usage, as a substitute for other solvents in degreasing and coating operations it may well become the largest source of stratospheric chlorine." [NAS, 1979b, p. 45].

Further information on the potential effect of methyl chloroform on stratospheric ozone is available from an EPA sponsored conference [EPA, 1980b] specifically on this subject.

It is arbitrary and capricious to include in the ANPR proposal CFC-22 and all other commercial and as yet uncommercialized CFCs (for many of which there does not exist quantitative information opposite any threat to the ozone - See section 3), and simultaneously exclude methyl chloroform for the same reason -- especially in the face of information available to the EPA from its own conference on methyl chloroform, and the NAS' expressed concern that methyl chloroform may well become the largest source of stratospheric chlorine.

Scope of Proposal

A quantitative illustration of the arbitrary nature of EPA's proposal is developed below, in Table 1. Utilizing the concept of relative ranking of compounds by their potential effect on stratospheric ozone ("ozone depletion potential" or permit pounds - See Appendix G), the potential threat to stratospheric ozone is compared for CFC-11, CFC-12, CFC-22 and methyl chloroform. It is seen that the calculated relative ozone depletion potential of methyl chloroform is three times that of CFC-22 (0.09 compared to 0.03). When total world releases of the compounds are figured in, methyl chloroform presents a potential threat to the ozone about 20 times that of CFC-22.

Table 1

Calculated Depletion Potentials and Relative Calculated Environmental Impacts for Selected Halocarbons

Compound	Relative Depletion Potential	1977 World Release (10 ⁶ pounds)	Calculated Relative Environmental Impact (Relative depletion potential x world release)	Relative Environmental Impact (Ratio to CFC-22=1)
CFC-11	1.0 (a)	674	674	156.7
CFC-12	0.84 (a)	830	697.4	162.2
Methyl Chloroform	0.09 (b)	930	83.7	19.5
CFC-22	0.03 (a)	144	4.3	1.0

(a) Calculated by Du Pont - see Appendix G.

(b) Calculated by Du Pont in a manner identical to that described in Appendix G for CFCs. The atmospheric lifetime of methyl chloroform in those calculations was 8 years.

3. JUSTIFICATION FOR PROPOSING TO CONTROL ALL CFCs?

EPA states in the ANPR:

"EPA believes that any regulation of ozone depleters should be as comprehensive as possible, consequently this regulation would address all CFCs." (emphasis added).

Notwithstanding that if the regulation is to be comprehensive methyl chloroform should not be excluded¹, we question the scientific justification for including all CFCs under the proposal.

Is EPA's belief sufficient or is technical support required? Technical support for EPA's proposed regulatory scope is not evident in the reference most often cited by EPA -- the 1979 NAS report [NAS, 1979a]. As EPA correctly states in the ANPR:

"NAS examined only two CFCs, CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorodifluoromethane) because they represent the vast majority of all CFCs produced." (emphasis added).

¹Part of our concern is that methyl chloroform competes in the marketplace with one of the CFCs proposed for regulation (CFC-113). Were CFC-113 to be regulated, many users would switch to methyl chloroform.

Scope of Proposal

In fact, none of the assessments of potential future stratospheric ozone depletion have included any CFCs except CFC-11 and CFC-12. Further, to our knowledge, CFC-113, CFC-114, CFC-115 (all included in EPA's scope) have never been thoroughly studied by EPA or others specifically opposite the potential of these compounds for ozone depletion. And CFC-22 has been given only a cursory examination -- acknowledged by EPA in the ANPR:

"NAS also briefly considered CFC-22 (chlorodifluoromethane) but excluded it from the analysis because as a partially halogenated compound, its likelihood of reaching the stratosphere before dissociating is much less than that of fully halogenated compounds." (emphasis added).

It is telling that EPA follows this statement in the ANPR with the statement:

"However, the findings by NAS on the ozone depletion potential of CFC-11 and CFC-12 are relevant qualitatively for all chlorofluorocarbons" (emphasis added).

Notwithstanding that no technical support is offered for this conclusion, we question the justification for a regulation based on a qualitative finding. To what extent will EPA's proposal reduce the alleged risk from CFCs -113, 114, 115, and 22? No risk determination has been made for any CFCs except CFC-11 and CFC-12.

Without study of the potential effect on ozone from all CFCs, any regulation must focus only on CFC-11 and CFC-12 (the only CFCs studied), although as we note elsewhere (Sections III, IV and V) even the extensive studies of CFC-11 and CFC-12 performed to date do not support a finding of unreasonable risk from these compounds.

An even more bizarre aspect of EPA's proposed "shotgun" approach is that the Agency's formula ($C_nCl_xF_yH_{2n+2-x-y}$; $x > 0$,

Scope of Proposal

$y > 0$ to bound the regulatory scope goes to extreme limits. A rigorous following of this formula would mean that even high molecular weight polymeric compounds would fall under the proposed regulatory restrictions if they contained any trace of chlorine (x is defined as > 0 and n is unlimited) even though these materials are nonvolatile with no potential for CFC emissions.

Last, the proposed regulatory scope would include a number of compounds which, through their potential future use, could provide part of the solution to the problem (if it exists) of ongoing use and emissions of potential high risk CFCs such as CFC-11 and CFC-12. This is discussed in the next section.

4. COUNTERPRODUCTIVITY OF PROPOSING TO CONTROL POTENTIAL FLUORO-CARBON ALTERNATIVES -- WHY REGULATE A POTENTIAL SOLUTION?

Not only is there little or no current scientific or risk justification for any potential regulation of CFCs to extend beyond CFC-11 and CFC-12, but the broad proposal in the ANPR to include "all alkanes that contain at least one chlorine and one fluorine, including CFC-11, CFC-12, CFC-113, CFC-114, CFC-115 and CFC-22, as well as several other CFCs not presently manufactured or manufactured only in very limited quantities" embarks EPA on a course that will impede and limit the development and application of potential alternatives to the currently used CFCs thought to present the greatest risk.

As an example, in Section VIII and Appendix B, we note that CFC-22, CFC-141b and CFC-142b show technical promise as refrigerants or blowing agent replacements for the currently used CFC-11 and CFC-12 -- replacements which due to a different chemical structure would drastically reduce the potential for stratospheric ozone depletion. However, by including these compounds in its regulatory scheme, EPA has severely reduced incentives to develop or use these compounds as replacements in the aforementioned CFC-11 and CFC-12 uses.

Again taking CFC-22 as an example, we showed in Appendix G that a pound of CFC-22 was approximately only 1/34 the potential risk to the ozone of a pound of CFC-11 and only approximately 1/29 the potential risk of a pound of CFC-12. Were the need to arise, even partial substitution of CFC-11 and CFC-12 by CFC-22 could reduce several-fold the risk to the ozone.

Scope of Proposal

Consistent with this objective, EPA states in the ANPR it would structure regulation "...in such a way as to provide incentives for industrial users to shift from those CFCs [hypothesized to be] most harmful to the stratosphere toward those CFCs posing a lesser [theoretical] threat." Yet the Agency's proposal does not create the incentive to use CFC-22 (as an example) so much as it creates a disincentive to use it, because it too is being regulated. So long as a potential alternative like CFC-22 is under the proposed overall cap on CFC production, users will be reluctant to convert to its use due to uncertainty over whether it would be further restricted in coming years. (See Section VII). If the Agency desires to create an incentive for users to convert from CFC-12 to CFC-22 (a step yielding an approximate 29-fold per pound decrease in potential risk to the ozone), CFC-22 should be exempted. Other reasons for exempting CFC-22 are provided in other parts of this Appendix.

In a recent letter from EPA to a Congressional representative [Wellford, 1980] it was stated:

"The Agency is studying methods to stimulate the development of substitutes for all [CFC] applications...."

Not only are we not aware of any such studies but what the Agency has proposed creates a disincentive to use potentially satisfactory alternatives, not a stimulus.

5. JUSTIFICATION FOR NOT EXEMPTING NON-EMITTING CFC USES FROM THE PROPOSAL?

In its ANPR summary of the ozone depletion theory, EPA states:

"The continued worldwide release of CFCs is therefore troublesome...." (emphasis added).

and uses as a Section heading:

"The Risks of Continued World Chlorofluorocarbon Emissions" (emphasis added).

Through all reports and discussions on the issue to date, it has been understood that the use per se of CFCs posed no problem to the stratospheric ozone layer, but that emissions of CFCs (from products and processes) which eventually were transported into the stratosphere were of concern. This is inherently obvious. The potential problem is in the stratosphere. Therefore, only those CFCs reaching the stratosphere are of concern. Refrigerators and auto air-conditioning systems do not get into the stratosphere. CFC emissions from these and other uses may.

Further support for the logic for exempting non-emitting uses may be found:

- In the Rand Report (in its discussion of economic incentive approaches to regulation):

"The only exemptions from the tax that would be recommended by efficiency and effectiveness criteria would be for CFCs used in applications where there are no emissions, such as when the CFC is used as a precursor for producing other chemicals that do not deplete ozone." [Rand, 1980, p. 240].

Scope of Proposal

- And even more tellingly, in EPA's Development Plan - "Chlorofluorocarbons - Phase I" [EPA, 1980e, p. 8]:

"Some CFCs are used as intermediates in the manufacture of non-ozone depleting substances. This use of CFCs should probably only be controlled to the extent that CFCs are released during the process."

Yet inexplicably, the ANPR does not provide for the exemption of non-emitting CFC uses -- in fact, does not even make mention of them.

The major CFC use resulting in no emissions is CFC-22 as an intermediate in the production of fluoropolymers. The end products are not potential ozone depleting substances. Therefore, this CFC use should be exempted from the proposals and all assessments and projections of production, use and emissions should exclude this and like CFC uses.

6. SUMMARY

- Any proposed rule should be restricted to CFC-11 and CFC-12 because:

a) There is no technical support for EPA regulating all CFCs when all technical studies to date have restricted their assessments to CFC-11 and CFC-12. Further, EPA has made no risk assessment of the potential effect on the ozone of any CFCs except CFC-11 and CFC-12, nor demonstrated how the proposed rule would reduce risk from these other compounds. CFC-22, in particular, presents a very small potential risk compared to CFC-11 and CFC-12.

b) EPA's proposed rule scope would cover all technically promising fluorocarbon alternative compounds. This creates a disincentive for further development and will restrict potential use -- results which are counterproductive to the Agency's stated goal of reducing the use of potential high risk CFCs (e.g., CFC-11 and CFC-12) through the creation of a stimulus to encourage the development and use of substitutes for CFC applications.

c) The use of CFCs which result in no emissions, such as the use of CFC-22 as a chemical intermediate, pose no potential threat to the ozone layer and, therefore, should be excluded from any further regulatory consideration.

- There is no justification for EPA regulating CFCs while ignoring the ozone depletion potential of other compounds, such as methyl chloroform.

X. APPENDIX I

ECONOMIC INCENTIVES
REGULATORY OPTIONS

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1. INTRODUCTION

Our ability to take a stance on economic incentives regulatory options is limited due to the newness of these concepts and the unavailability to date of adequately detailed potential structures on which to base our analysis.

We agree there are numerous problems and inefficiencies associated with traditional command and control regulations as they have been imposed historically. And many of the theoretical arguments advanced in support of the economic incentives approaches are appealing, at least at first glance. However, once one progresses beyond a theoretical or conceptual examination of the incentives options, it becomes obvious that they too have practical limitations. Careful consideration of design, implementation and administration issues reveals that these concepts, while seemingly efficient and simple at face value, have associated with them complex policy problems and questions.

From our examination to date, we are concerned there are numerous and interrelated legal, hidden cost and efficiency problems associated with the potential implementation and administration of these concepts. There also is a natural reluctance to commit one's business to the experimental evaluation of untested theoretical concepts. Regulation often has produced results and inefficiencies not readily foreseeable from pre-application examination. It follows that any new regulatory intervention ought to be carefully thought out before it is implemented. As an example, even if incentives policies result in less of a straight-jacket than direct controls (as theorized), nevertheless they can be applied in a way that would leave society worse off.

In the chemical industry, we require that theory be put to test; first on the lab bench, then in a pilot plant or test market, prior to committing to full scale product or process

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introduction. We question the wisdom of jumping from economic theory to real world fluorocarbon production and use without first obtaining some practical experience with these concepts in an area with much less potential impact. When the economic, energy conservation and safety importance of CFC products are considered, the wisdom of such an action is further questioned. The concepts should be tried out on a limited basis and the experience assessed before committing to the full scale-up which fluorocarbons would represent.

We also have a fundamental concern over the potential broad-based implications of this form of regulation to the balance between business and the regulatory arm of government. It may be argued that these concepts minimize regulatory control of industry and are economically efficient through their reliance on the operation of the marketplace. But the use of these concepts represents a potential for ever-increasing control in an area heretofore the province of business and the consumer. Pollution control is a well defined area in which business, government and environmentalists seem to be progressing towards a workable balance. Policies -- no matter how theoretically sound, or well intentioned -- which potentially expand this arena into economic control of the marketplace, should be examined carefully and approached with caution.

The analyses we have seen to date provide more questions than workable solutions. We feel that neither EPA nor Rand have addressed adequately the areas of policy design, implementation and administration, or their implications (although the Rand researchers do identify many of the potential problem areas and suggest substantial further work).

Part of the problem we experience is the lack of adequate option detail for analysis. Without detail which addresses identified questions and concerns, it is extremely

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difficult for us to perform the required analysis from our perspective. Until specific detailed proposals are developed which would allow the evaluation of the legality, difficulty and costs of complying with incentives options compared to traditional command and control options, we must hold our opinion or "preference" in abeyance. The potential problems must be addressed publically by EPA, though the creation of detailed hypothetical option designs, with allowance for comment by industry and other interested parties, prior to implementing any of these options.

2. BACKGROUND

The following presents our understanding of the problems with mandatory controls, the "why" and the "how" of economic incentives controls, followed by some of the arguments against incentive options. Our comments in the following sections are based upon this understanding.

a. Mandatory Controls

Mandatory controls, or command and control options, are the basic technique used over the last decade to regulate air and water pollution. They are targeted at particular activities in individual industries.

It is argued that these options are cost inefficient in attaining environmental goals such as CFC emissions reduction due to inherent inflexibility. Some activities regulated by mandatory controls may require large expenditures to reduce emissions by modest amounts, whereas other activities, if given the same expenditure, would show large reductions. Further, under such controls, the cost per pound of emissions reduced may rise rapidly for a given activity as the control standard is approached, whereas a comparable expenditure in another activity could produce greater reductions.

Yet, under command and control options, industries or individual firms within the targeted industries could not transfer expenditures between each other (either inter- or intra-company or industry), in order to attain the greater efficiencies in emission reduction versus cost available elsewhere.

An additional concern with mandatory controls is the problem of enforcement. Regulations targeted to specific emissions activities within specific industries must be enforced

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at the point of control. In the case of CFCs, this could mean enforcing standards in thousands of use locations.

It also is argued that once a firm has met a control standard there is no incentive for the firm to reduce use beyond the standard, nor for competitive reasons, to spend monies for innovation which would lead to lower use.

b. Economic Incentives Options - The "Why" and the "How"

In recognition of the limitations of command and control options, economists have long argued for the use of economic incentives policies. These policies are theorized to function by effectively raising the prices users must pay for their polluting activity, thus making the control of the activity economically attractive.

In the case of CFCs, were the cost of using them to be higher due to a regulatory policy which increased their price, users would seek ways to reduce their purchase and/or to use them more efficiently. Use reduction could be achieved through product or process substitution or increased conservation, and use efficiency could be increased through recapture and reuse.

Under these options, the degree of use or emission reduction desired could be controlled simply through adjustment of the economic penalty imposed on the chemical's use. At higher cost penalties, firms would find it attractive to make greater expenditures to further limit the use of the chemical. Theoretically, the optimal point of economic disincentive on the use activity would be the premium at which an increase in the cost of reducing the use would be equal to the decrease in the environmental damage that would result from the chemical's use.

Economic Incentives Options

Once the desired policy outcome is decided upon, the policymaker could step back and limit further involvement to a monitoring of the degree of goal attainment, followed by an adjustment (up or down) of the use premium as needed to meet the preset goal. This would minimize the need for direct monitoring and enforcement of controls on the behavior of individual firms and industries.

More importantly, it is argued that such a scheme would allow the individual firms and industries to decide upon the most economically sensible course of action for their circumstances. Some, lacking the technology or resources to make much headway in the use reduction, would pay the penalty. Others would find it attractive to substantially reduce their use to avoid the penalty, often going beyond any standard set under command and control.¹

In short, it is argued that under such a system, firms will operate in their own best economic interests with the net result that the overall use or emissions goal will be met more efficiently -- i.e., at lower cost -- than would be the case under a system in which specific steps or controls were required without consideration of the individual capabilities and motivations of those affected.

¹This is because command and control steps generally are set at some average point of technological and economic achievability so as not to be so stringent that they prove unworkable or result in massive business failures.

Economic Incentives Options

The two incentive policies most often discussed are taxes and quotas. A tax would be imposed on the use of CFCs, resulting in the user paying the CFC producer the normal supply price plus a tax penalty for each pound of CFC purchased, thus creating an incremental incentive (determined by the size of the tax) to reduce the use of the chemical. The control agency would raise or lower the tax in response to the quantity of CFC purchased, relative to its policy goal.

A quota system would start from the supply side of the equation. If a quota on CFC production or sale were imposed, some sort of premium price mechanism would evolve to allocate the reduced amount of CFCs among the competing uses. Whether the producers themselves effected this through price increases, or the users through buying and selling permits for the right to purchase the limited quantity of CFCs, makes little difference in theory. The net effect would be that the effective price of using CFCs would increase, thus creating an incentive to reduce their use. Many theorists favor the latter approach, terming it a "marketable quota system." The users would market among themselves the permits for CFC purchase. The permit price would reflect the supply availability and serve to allocate the limited CFC among the uses based on value-in-use or essentiality. The control agency would simply raise or lower the production or sales quota of CFCs to meet its policy goal.

Theoretically, the same reduction in use, at the same cost, could be achieved using either permit quotas or taxes -- i.e., for a given use reduction goal, either option should result in the effective increase in CFC price being the same, thus reducing CFC use by like amounts. However, it is important to note that the theoretical equivalence between taxes and quotas is dependent on markets being purely competitive and on quotas not being used to reduce competition. [See section 4-d].

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c. Arguments Against Economic Incentives Options

Many of the concerns raised about the use of economic incentives regulatory options result from the absence of detailed descriptions of how these options would work and an understandable reluctance to have untested, theoretical concepts applied to important industries. Prior to satisfactory resolution through option design and trial testing, these concerns remain arguments against the use of economic incentives approaches.

i. Double Burden

Any system which required the paying of a charge (taxes or permit bids) would remove monies that would otherwise be used on emission control.

It takes time for a firm to analyze its abatement possibilities, design or decide on new equipment, and place in operation new technology. Given the need for this lead time, any charge applied the first few years would be a double burden: money would have to be spent for the incentive charge, even though there may be no reasonable action a firm could take to reduce its emissions in this period; and monies would have to be spent in this period for steps to reduce emissions over the long run.

As a solution, the gradual phase-in of incentives options, to allow industry time to effect emission reduction steps before having to pay a penalty, has been suggested. We believe all regulations should be phased-in over a reasonable time frame in order to minimize the economic impact of compliance.

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ii. Small Firm Argument

Those firms too small to afford emission reduction equipment would still have to pay any charge, but without any potential for eventually offsetting the charge cost through emission reduction. The net result is that these firms pay more for doing what they have always done -- but this increased cost would not be offset by any reduction in emissions, immediate or longer-term. Consequently, small firms' costs would increase relative to other firms. This would have the effect of shifting demand away from small firms towards other firms and, in the extreme case, put the smaller firms out of business.

One suggested solution is to exempt small firms from a charge system. But exemptions would significantly complicate the very design and enforcement attributes which make the incentives options attractive. Once the regulatory agency begins granting exemptions, an incentives policy is likely to lose its theoretical property of achieving any desired reduction of CFCs at the lowest achievable compliance cost.

iii. State Versus Federal Requirements

The primary argument for economic incentives options is that if an economic disincentive to pollute is created, individual firms, acting in their own best economic interests, collectively will reduce polluting activity much more efficiently than were each firm to be required to meet set control standards. Were such a system in place on a Federal level, but individual States still allowed to issue traditional command and control regulations, the economic efficiency of the incentives option could be destroyed. The Federal system would be designed to permit firms to reduce emissions in the manner and to the degree economically justified. Yet State issued command and control steps could significantly undermine this economic rationale. For

instance, a firm could be required by the State to put in equipment making no economic sense to the firm, yet then have to pay a Federal charge penalty for not having made the best economically justified decision.

It is an overstatement to say that Federal and State controls would present a strictly additive burden because a State command and control reduction regulation would reduce the Federal charge payments. However, there would be the potential that the State regulations would partially negate the very efficiencies touted for the incentives approach. Clearly, harmonization of Federal and State options must be carefully examined.

iv. Transfer Payments Create Inflationary Pressures

It is argued that taxes or permit fees to government by industry are simply transfers of wealth within the economy. Since such payments do not use up real resources and are eventually returned to the economy, it is claimed they do not directly contribute to inflation. This argument is supported by the formal definition of inflation which relates it to an expansionist monetary policy.

However, these transfer payments would represent a real cost of doing business to industry and would be reflected in product prices. Consumers equate price increases to inflation and social pressure for increased wages would result. If this pressure exists under a monetary policy that does not restrict the money supply, the price increases caused by the charges indirectly lead to inflation.

v. Political Problems

- A tax or a permit fee system could be subject to political manipulation. Due to the flexi-

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bility built into these systems (to allow adjustment up or down in response to the degree of attainment of the environmental goal), significant changes in fee structures could be much more easily made than altering mandated control steps.

- Depending upon the ultimate fate of the monies collected under a charge system, revenue addition is a concern. How easy would it be to decrease the charge in response to a lessened environmental problem or an overattainment of goal were various programs or funds dependent upon an anticipated revenue level?
- Transfer payments are potentially a very sensitive political issue. If the system employed does not compensate for the charges, total regulatory costs are far greater for an economic incentives policy than for mandatory controls. This destroys the theoretical benefit of economic incentives options -- lower cost.

If the system is designed to compensate for the charges in some manner, the politically sensitive issue of distribution of wealth among the CFC users, industry or public, must be addressed. Who pays, who gains and on what basis?

vi. Legal Problems

There are two types of legal concerns that must be addressed. These are discussed in detail in 5-c below and in Section III - Legal Considerations, so will only be touched on here:

- It arguable whether the EPA has the authority under current law to implement a marketable permit system, depending upon how it were designed. Additionally, administrative agencies have no constitutional authority to levy taxes.
- Proponents of economic incentives tend to minimize the legal implications of first, the proposed option designs and implementation schemes, and second, of the anticipated activities and responses of firms under a charge system. However, it may not be legal for firms to comply with some of the proposed options.

To study the implications of economic incentives options, EPA contracted with the Rand Corporation to analyze the efficiency and impact of these options opposite traditional command and control regulations if both forms were to be applied to the goal of reducing CFC emissions. The balance of this Appendix centers on our assessment of the thoroughness and validity of Rand's and EPA's (from the ANPR) assumptions, analyses and conclusions for the potential use of economic incentives regulatory options in the control of CFC emissions.

We have roughly grouped our comments into three areas. Section 3 considers how some of the procedures used by Rand to

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estimate the costs of alternative regulatory policies may influence the report's conclusions. Section 4 focuses on Rand's and EPA's treatment of the economic incentive policy designs and their implications. Section 5 deals with the implementation and administrative issues associated with the use of incentive options. Overlap in certain areas is unavoidable.

A preview of our comments is offered by three basic propositions:

1. Rand's analysis of economic incentives regulatory options is incomplete. Administrative costs of the policies are not quantified and the analysis of control options is incomplete.

2. The Rand Report pays insufficient attention to legal considerations, such as the danger that a permit system could be used to attain monopoly power in the market for CFC.

3. As a consequence of EPA's definition of the scope of the study, Rand limited its analysis to estimating the cost of alternative modes of regulating CFC. By failing to address the broader question of the net benefits that could be attained under each policy option, the report fails to consider factors that can have an important bearing on which policy alternative is preferable from society's viewpoint.

3. RAND'S ESTIMATING PROCEDURES

a. Data Uncertainties

There remains considerable uncertainty about the cost of CFC regulation. As a result, the cost advantage of incentives policies over direct controls could be greater or smaller than estimated by Rand. As significant error in predicting compliance costs could lead to (a) adoption of an inferior means of regulating CFC and (b) a policy target that is unwarrantedly stringent or lax.

A policy that restricts the use of CFCs must result in either substitution by consumers of final products that make less or no use of CFCs, or substitution by firms of other inputs for some of the CFCs presently being used to produce final products. In the absence of perfect substitutes for CFCs, these substitutions will impose costs on consumers and firms.

Since perfect substitutes for CFCs do not exist, any regulatory policy that leads to a less CFC-intensive production technology will result in some increase in the real resource cost of production. The size of the cost increase will depend loosely on the ease of replacing CFCs with other inputs (a technological issue) and the volume of output affected by the substitutions (a matter of the size of the market traditionally involving use of CFCs). To estimate the costs imposed on firms by CFC regulation, information is needed on the size of markets for goods involving CFCs and the production cost of these goods by alternative technologies using less CFCs.

These information requirements impose serious difficulties. Historic data is limited and may not be very accurate. Projecting future uses of CFCs involves further

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uncertainties. Continuing evolution of the uses for CFCs and the technologies involved, adds further complication.

Rand has dealt with these uncertainties by attempting to develop a working knowledge of the role played by CFCs in the production of final products and, based largely on engineering estimates, the scope and cost of possible substitutions for CFCs in those production processes. These estimates, combined with the assumption that firms will always seek to minimize their production costs, provide the basis for Rand's estimation of the compliance costs of each regulatory strategy.

However, considerable uncertainty remains about the true compliance costs of CFC regulation. A key source of this uncertainty is that Rand seems to have only limited knowledge of the nature of end products dependent upon CFCs. A further source of uncertainty is Rand's assumptions concerning substitutions that can be made for CFCs.

The significance of these data uncertainties is that the true compliance cost could be significantly higher or lower than estimated by Rand. Hence, the cost advantage projected for incentives policies could be either under- or over-estimated. If incomplete information led to overlooking a direct control that would substantially reduce CFC at a modest cost and could be easily enforced, the compliance costs of direct controls would be overestimated relative to an incentive system. On the other hand, if the cost of reducing CFC use has a wider range across user industries than estimated by Rand, the cost advantage of an incentives policy would tend to be underestimated.

A significant error in estimating compliance costs can have important effects on policy formulation. If the implementation costs of taxation, marketable permits and direct controls were the same, choice of the best policy alternative

would depend simply on the ordering of policies by compliance cost. Errors that did not affect the ordering would be inconsequential. But if, for example, direct controls are expected to be less costly to implement than a permit system, the accuracy of compliance cost difference becomes important.

Once a form of regulation is selected, compliance costs become relevant to the determination of the socially appropriate reduction in CFC emissions (which should be the objective of regulation). Consequently, although Rand focuses only on the relative cost-effectiveness of the policy alternatives, the accuracy of their cost estimates is also relevant to selecting this appropriate degree of control. The potential optimal curtailment of CFCs is inversely related to the potential cost to society of reducing the uses of CFCs, so the larger the compliance cost, the smaller the reduction in CFC use that the regulatory policy would attempt to accomplish. This means that an underestimate of compliance costs could lead to more stringent regulation than would be socially desirable, and vice versa.

b. Discounting Procedures

The report measures the effectiveness of a regulatory policy by its predicted curtailment of CFC production over the period 1980 to 1990. Ignoring the effect of a policy on year-by-year production (and thereby emissions) is justified in the report by two arguments. First, the effect on the ozone layer is relatively insensitive to different time profiles of the same volume of cumulative emissions. Second, the time-lag between CFC production and the full effect of emissions on the ozone layer is long. Thus a policy that delays emissions within a decade results in a relatively small delay before the full effect on the ozone layer occurs. Since the report ignores the time profile of

CFC reduction, all policies that produce the same cumulative reduction over the decade beginning in 1980 are represented as being of equal value to society.

This treatment of benefits is inconsistent with the way costs are calculated in the report. The compliance costs estimated for each year are discounted back to a base year and represent the present value of all costs incurred in accomplishing the cumulative reduction in CFC production over the decade. This discounting procedure recognizes that a real dollar of goods is worth more today than tomorrow. Inconsistency arises in the report's failure to discount the flow of benefits in a similar way.

Although Rand suggests that the benefits from reduced CFC emissions are relatively insensitive to their time profile, that will not necessarily be so. Consider an extreme example, for some stipulated cumulative CFC reduction over the period 1980-1990: all the reduction occurs in the first year under policy A while all the reduction occurs in the tenth year under policy B. The benefits from policy B will lag those from policy A by 9 years. At the 11 percent rate of discount used by Rand the present value of benefits produced by policy B will be $1/(1.11)^9$, or about 40 percent of the value from policy A.

The report states that a constant tax rate over the decade will produce a time profile of CFC use paralleling that from direct controls. If the difference is negligible, the failure to discount benefits does not interfere with a comparison of the merits of the policies. But the report also considers a tax that is initially set at a lower level and increased uniformly over the decade, producing equivalent cumulative reduction in CFC use. Failure to discount benefits introduces an

error in comparing this policy to others. The policy is credited with a lower present value of compliance costs, but the present value of benefits also would be reduced by the delay.

c. Administrative Costs of Regulation

Public sector expenditures for developing, implementing and enforcing regulation of CFCs are not included in Rand's estimates of regulatory costs. Since these expenditures constitute real resource costs, their omission tends to understate the real cost to society of regulating CFCs. Because both the information required to formulate a particular policy and the cost of enforcing it will be different for mandatory controls, taxation, or a permit system, administrative expenses must be included to correctly determine cost-effectiveness, as well as to assess correctly the total cost of regulation.

Administrative expenses are difficult to estimate because, to a considerable extent, they reflect discretionary choices. The amount of information a regulatory authority elects to acquire in the process of setting and enforcing policy will affect both the cost and the quality of regulation. If there were simple decision rules to determine the economically efficient amount of information for a regulator to obtain, the administrative costs of regulation could be estimated on that basis. Since this is usually not the case, administrative costs are difficult to anticipate.

But failure to take into account administrative costs can lead to two types of regulatory errors. First, if the selection of a policy to regulate emissions is based exclusively on the private sector compliance costs, the chosen policy may not be the one minimizing the full cost of regulation -- private and public sector costs. Second, regulation which appears attractive when only private sector costs are compared to benefits may be

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undesirable when the administrative costs of regulation are added. This can mean either that no regulation would be preferable or, when administrative costs rise with the stringency of regulation, that the curb on emissions is tighter than would be in the public interest.

It is argued that a tax or a quota should be less costly to administer than a system of direct controls. This implies that Rand's omission of administrative expenses results in an underestimate of the cost advantage of incentives policies. However, there are myriad unanswered questions and concerns relating to implementation and administrative issues for economic incentives options [See section 6]. Design of these options to accomodate these concerns undoubtedly will result in more complex regulations than the theoretical ideal, leading to an increase in development, implementation and enforcement costs. Costs could even rise to the level of mandatory controls, depending upon the complexity of the modifications required. Another consideration is that in the case of CFCs, substantial information on which to base mandatory controls already is available.

Enforcement costs can be avoided entirely at the risk of substantial noncompliance with the regulations. Alternatively, a regulatory agency can police the affected markets sufficiently to insure that compliance is complete, resulting in substantial enforcement costs. Actual enforcement costs will depend on the ease of enforcing the selected mode of regulation and on the degree of enforcement chosen.

The Rand Report implicitly assumes that enforcement of each of the policy alternatives will be complete, and that enforcement costs of incentives policies will be minor. It is our view that Rand is somewhat glib in characterizing enforcement costs of incentives policies as minor. Either a permit system or taxation could create a substantial incentive to evade the

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regulation of CFC use, necessitating enforcement comparable to that needed with mandatory controls. Additionally, as incentives options become more complex (in order to address all the design and implementation concerns), more enforcement will be needed. An example would be the case of an incentives option with exemptions.

Therefore, since the cost of enforcement may be substantial for either incentive option, it certainly merits more careful attention than Rand seems to have given it.

d. Impact of Uncertainty on Choice of Optimal Incentive Design

Rand points out, that an important distinction between quota and tax options results from the fact that there is some uncertainty about the estimated demand schedules used to predict the permit price or the requisite tax to achieve a given policy goal. Under permits, the level of CFC use is known with certainty, but the permit price that actually develops might differ from the prediction; under taxes, the increase in CFC price is known with certainty, but the reduction in CFC use that occurs might differ from the prediction. Thus the earlier discussed theoretical equivalence (same reduction in use at the same cost) of the incentives policies is dependent upon perfect information of CFC costs and demand. Since perfect information is not available, the extent to which these are relative uncertainties in the information on the demand for, and costs (production and social) of, CFCs should dictate, at least in part, a choice between incentives options. Consequently, a choice between taxation and a permit system should depend in part on whether the regulatory authority has a clearer notion of the appropriate tax on CFCs or of the appropriate quantity.

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Rand's assessment of alternative methods for regulating CFCs is limited to a consideration of the cost of obtaining a designated reduction in CFCs under each policy. This, however, is not a sufficient criterion to determine the best choice among policy alternatives. If the degree to which it is socially optimal to reduce CFC emissions is uncertain, the best mode of regulation will not necessarily be the one that is most cost-effective. As an example, if there is more uncertainty about the correct tax level than the appropriate reduction in emissions -- but a permit system is felt to pose a danger of market concentrations -- then the best solution might be direct controls, even though theoretically more costly.

Last, significant uncertainty about the demand for CFC, its production cost or the damage from CFC emissions can lead to the public being worse off under any of the policy alternatives than if CFCs had not been regulated.

4. OPTION DESIGN IMPLICATIONS

a. Designs Should Reflect Different Potential Environmental Impacts of Compounds

Different fluorocarbons have greatly different potential stratospheric environmental impacts. Some (CFCs) are of high concern; others (hydrogenated CFCs) of moderate to low concern; and others (FCs containing no chlorine) of no concern. Economic incentives options should be designed to reflect these differences through a quota or fees system which penalizes least the use of the compounds of lowest environmental concern. This would focus emission reduction efforts on the compounds of greatest risk, and encourage replacement of high risk CFCs, e.g., CFC-11 and CFC-12, with low risk substitutes, e.g., CFC-22 or CFC-142b.

EPA's system of "permit pounds" is a step in the right direction. However, as discussed in Appendix G. EPA has made some errors in its system.

The concept of relative environmental risk could be applied equally well to taxes (through setting different tax rates by compound) or to marketable permits (through setting a quota of the total permissible stratospheric chlorine burden from CFCs and relating a permit unit to "ozone depletion potential" rather than to pounds of CFC emissions). Under this scheme, different compounds would have different permit values.

As an example, using our figures from Appendix G, industry would have the choice of producing 34 pounds of CFC-22 or one pound of CFC-11, since both would account for equal units of potential for ozone depletion. The net result would be both more efficient regulation (as it would control directly the

environmental risk factor) and cost-effective regulation (as it would allow industry substantial flexibility in production and use).

b. Design Control Point - Production, Use or Emissions

There are a series of considerations relating to the impact or control point of incentives options. Although EPA discusses a number of the possibilities in the ANPR, neither their identification nor analysis of the different approaches is thorough. What is needed is an ordering of all the possibilities with a discussion of the pros and cons of each. After the initial questions of "What are we trying to control?" and "How much control is needed?", are answered, a series of complex, interrelated questions must be addressed. A representative sampling of these and how they might be ordered follows:

- Should control be imposed on users or producers?
 - a. If on users, should control be on CFC emissions or CFC use?
 - i. If on emissions, what are the enforcement problems?
 - ii. If on use, should all users be taxed the same and have an equal opportunity to acquire permits, or should taxes or permits vary by application? Should there be exemptions for certain uses (e.g., where no emission reduction is possible or where no emissions occur) or for certain users (e.g., small firms which would otherwise be forced out of business)? What are the problems associated with exemptions?

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- b. If on producers, will there be legal problems?
What is the potential for restraint of trade?
- How should control be imposed?
 - a. Should permits initially be put up for bid or allocated?
 - i. If put up for bid, who can bid and on how many?
 - ii. If allocated, on what basis? Who will be eligible? What about new entries?
 - b. How should reclaimed material be treated?
- How would imports be handled?
 - a. If taxes, what would be the repercussions?
 - b. If permits, would imports have to fit into United States permit quotas? If so, how?

EPA is proposing to use economic incentives concepts. It is EPA's obligation to think them out and present proposals which address these and related questions. EPA's approach to date has been to ask industry to answer the questions rather than EPA doing the necessary work to support its proposals.

In the ANPR, EPA proposes to regulate either the production or the use of CFCs, not the emissions. However, regulation of CFC use or production will not produce outcomes exactly equivalent to the direct regulation of emissions. And it is the emission of CFCs which leads to the potential environmental damage, not the production or use.

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When two products, one of which poses environmental hazards, are unavoidably produced in fixed proportions, regulation of the output of either product can be used to curtail environmental damage. The choice between the hazardous product itself or the product rigidly linked to it may not be important unless the cost of enforcement differs.

If, however, the proportions in which the two products are produced can be varied, a policy that regulates the harmful product indirectly, by acting on the closely related product, can lead to subtle inefficiencies because the relationship between the two products is elastic. EPA fails to note this distinction. The area requires further examination.

Further, a key advantage to regulating CFC emissions directly -- that could be lost with indirect regulation (taxes on use or use permits) -- is that under direct regulation of CFC emissions, only emissions are penalized. CFC-using activities which do not result in emissions, properly, are not penalized.

c. Transfer Payments

A critical concern with economic incentives options is over the size, control and fate of the monies collected. For simplicity, this problem can be approached three ways: i) ignore compensations; ii) reduce the size of the transfer payment (without undermining the economic incentives to reduce CFCs); or, iii) compensate those hurt by the payments.

i. Uncompensated Transfer Payments

Rand estimates that transfer payments generated by economic incentives options for even their moderate "benchmark"

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reduction in emissions will be approximately \$1.5-1.7 billion, a number many times in excess of the option's compliance costs. A quote from the report succinctly sums up this problem.

"Under an uncompensated economic incentives policy, cumulative transfer payments would be very large, ranging upward from \$1.5 billion for the least costly benchmark-equivalent policy. For the firms that pay them, uncompensated transfers dwarf the costs of reducing emissions. On average, a firm's expenses for transfers under an uncompensated benchmark-equivalent policy are about fifteen times the costs of actually reducing emissions. For all but a few CFC-using firms, the total expenses under uncompensated economic incentives are greater than the compliance costs under mandatory controls." [Rand, 1980, p. 18].

Other problems with uncompensated transfer dollars are political. There is concern over the possibility of rate manipulation and revenue addition [See section 2].

ii. Reduce Transfer Payments

Due to the potential problems with transfer payments, Rand suggests a number of possibilities to reduce their impact. An obvious solution would seem to be to exempt users where CFC demand is relatively inelastic (because of use essentiality and the unavailability of emission reduction options), e.g., polyurethane insulating foam. But once exemptions are allowed, enforcement difficulties and costs increase markedly. For enforcement and other reasons, Rand discards the exemption approach.

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Instead, Rand suggests direct allocation of CFC use. This approach involves giving an initial allocation of permits, per period, to CFC users according to a regulatory formula, rather than requiring that users initially purchase permits. Even under this approach, however, the real cost of regulation is likely to be unnecessarily high because the cost of administering direct allocation of permits is likely to be considerably larger than the cost of distributing permits by auction. Further concerns are questions of allocation - what "regulatory formula" and what basis would be used for distribution? What allowances should be made for new uses or new users?

iii. Compensated Transfer Payments

Neither the benefits nor the beneficiaries of compensation are made entirely clear by Rand or by EPA. A key concern not addressed is that those who would benefit from compensation are not necessarily those on whom the primary regulatory burden would fall.

Throughout the study, it is assumed that demand for final products using CFCs is perfectly price inelastic. If so, user industries will be able to pass through to consumers any increase in cost due to regulation, whether its source is higher resource costs or transfer payments on taxes or permits. The burden of adjustment, measured by potential reductions of real income, would fall primarily on consumers of final products using CFCs, and workers and stockholders in firms producing CFCs. However, Rand focuses on compensation to user industries, as a result of relaxing the assumption that final product demands are perfectly inelastic. This leads one to consider the possibility that it may not be possible to pass all cost increases through to consumers.

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Of the policies proposed to nullify transfer payment impact, the one least likely to increase regulatory compliance costs would seem to be a free allocation of permits. Even this approach, however, is likely to result in higher real cost of regulation because of the cost of sorting our competing claims and administering a direct allocation.

Each of the other combinations of incentives and compensation considered by Rand appears to be capable of leading to serious cost inefficiencies. Consider, for example, the rebate scheme proposed in the report, which would involve simultaneously subsidizing final goods that make use of CFCs while taxing CFC use. If the demand for final products using CFCs is at all responsive to price, a policy that simultaneously taxes the input and subsidizes the output will result in a higher real resource cost of curbing CFC emissions than a policy that simply taxes the input.

In addition, if a firm knows compensation of payments will be complete (i.e., all the emissions taxes or permit fees paid will be returned to the firm), there will be no incentive for firms to reduce their demand for CFCs. This can be seen by noting that, under complete compensation, choice of less CFC-intensive technology makes a firm worse off than making no adaption to the charge. A firm that does not attempt to reduce its exposure to the charge by reducing the use of CFC would not be any worse off after regulation than prior to it, since the firm would receive compensation exactly equal to its payments. If on the other hand, it were to reduce its charge liability by substituting other inputs for CFCs, it would be worse off. This is because, although its reduced payments are compensated, the rise in its cost of production resulting from reduced use of CFCs would not be. If compensation for CFC payments is complete, therefore, no cost-minimizing firm will reduce its use of CFCs.

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Although complete compensation is an extreme example, the preceding analysis can be generalized in the form of two propositions. First, the effectiveness of a charge to reduce emissions will be limited under any scheme that makes the transfer of governmental funds to a firm a positive function of the firm's CFC charge liability. In addition, if a partial compensation scheme leads to firms forming differing expectations about the proportion of their payments that will be returned by the compensatory policy, the CFC reduction that does occur will not be accomplished at a minimum compliance cost.

Second, unless final product demand is completely inelastic, any scheme linking compensation to the output level of goods using CFCs will result in higher than necessary compliance costs.

Lastly, if one is going to compensate firms which would be affected adversely by an incentives policy, there is no obvious reason why compensation should not be made for compliance costs as well.

To sum up concerns about transfer payment compensation techniques, another quotation from the Rand Report is useful:

"The implementation issues associated with the design of compensated economic incentives policies should not be underestimated. Both the basis and the formulas for compensation raise politically sensitive and economically complex issues. They are politically sensitive because of their obvious and direct implications for the distribution of wealth among the CFC user and producer industries. They are economically complex because it is no simple matter to devise specific rules that prevent distortions in the policy that might thwart the economic incentives it is intended to create." [Rand, 1980, p.239]

d. Market Structure Effects of Regulatory Design

If markets are purely competitive, it should be possible to establish a quota in the form of marketable permits that will produce the same regulatory results as the imposition of a tax on a pollutant. However, when the markets affected by regulation are not purely competitive, the equivalence between taxation and permits breaks down. Under this circumstance, a permit system can have a variety of undesirable effects. As an example, when a firm's purchase of permits is sufficiently large to affect the price at which the permits are obtained, large firms will find it profitable to engage in more costly substitutions for CFCs than small firms. This would result in the compliance cost of attaining any CFC abatement target being greater than it would be when taxation is used.

The second broad problem of a permit system is that it may unavoidably lead to a greater reduction in the use of CFCs than would be socially desirable. This possibility arises under a permit system because the requirement to possess permits to produce (or use) CFCs could be exploited by firms to attain or enhance monopoly power in their product markets.

As an example, assume the quantity of permits issued by the government is equal to the socially optimal use of CFCs. If socially optimal production is smaller than the output level that would maximize industry profits, each firm will have a profit incentive to produce up to the limit of its permits holdings, regardless of the distribution of permits among producing firms. In this situation, therefore, although the distribution of permits probably will be of interest to each firm, it is of no obvious importance from the perspective of efficient regulation.

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If on the other hand, the socially optimal production of CFC were to exceed the aggregate output that maximized industry profits, a potential would exist for a firm to profit from hoarding some of the permits it acquired, rather than producing up to the limit of its permit holdings. In effect, permits could be used as a means of profitably restricting output, with the result that CFC use would be reduced more than would be in the public interest.

There are a number of devices that might be used to prevent a permit system from being used to increase industry concentration, but it is not obvious that any mechanism can be completely effective without at the same time adding further to the cost of regulation. Therefore, before adopting a permit system to regulate CFCs, the ways in which the system might lead to socially harmful industry concentration, and the steps that might be taken to mitigate such developments, should be carefully examined.

e. Risk Trade-offs

As with mandatory controls, economic incentives options imposed only on CFCs would result in emission reduction activities (e.g., product or process substitution) that bring with them other risks - to the worker, the consumer or the environment (See Section V - Risks). If the case made by Rand is correct that a "moderate" economic incentives level will result in more elimination of CFC emissions than mandatory controls, then the risk "created" by incentives options likely will be greater than that from mandatory controls. The degree of risk resulting from the imposition of any regulatory option must be compared to the risk the option is being employed to reduce.

f. Diminishing Returns

From Rand's summary of the potential for, and costs of, emission reduction under economic incentives options, it is clear that successive price increments of the same amount yield even smaller increments in emissions reduction. Further as the CFC price rises, compliance costs rise far more rapidly than reductions in emissions. The same situation occurs under mandatory controls -- the first pounds of a pollutant reduced are the cheapest.

What is worthy of comment is the steepness of the curve. Clearly, there are practical economic limits for incentives options. In addition, it should be noted that the steep rise in compliance costs excludes transfer payments.

5. OPTION IMPLEMENTATION AND ADMINISTRATION ISSUES

a. Uncertainty Concerns

The underlying uncertainty on regulatory costs and benefits [See section 3] will lead regulated firms to recognize the possibility that the initial policy may be subject to significant changes to correct for regulatory error. This leads to a second uncertainty issue.

One of the arguing points for economic incentives options is their flexibility, i.e., they can be rapidly adjusted in severity up or down to reflect a changing environmental risk or degree of policy goal attainment. Unfortunately, this very flexibility gives cause for concern.

If a tax or quota were adopted, there needs to be a rationale for the level imposed and for future possible adjustments. The rationale must be equally well understood by the regulators and regulated industries alike. Industry needs to know the parameters and logic of the system under which it must work if it is to plan and respond satisfactorily to the environmental objective. A control system should not be prone to dramatic swings due to vulnerability to political pressure or changing policymakers.

One of the attractions of command and control options is that they generally are established only after fairly extensive information exchanges, deliberations and challenge -- with the consequence that what ultimately is promulgated tends to remain in place sufficiently long that operational and investment decisions can be made with a reasonable expectation of payback.

"In contrast, firms may perceive tax rates or quota levels as highly variable, subject to regulatory whim or political manipulation. If so, firms might be reluctant to undertake long-term investments that would reduce emissions for fear that future regulatory action would make the investment obsolete or reduce its cost-effectiveness. Thus, establishing and maintaining long-range policy goals can contribute to the success of an economic incentives policy strategy." [Rand, 1980, p. 242].

The effect of uncertainty is also discussed in Section VII.

b. Mechanics of Implementation

Because there is little or no practical experience with economic incentives regulatory options as designed by Rand, the report left unanswered numerous "how to" questions. As noted elsewhere, EPA has not answered any of the questions in its economic incentives proposals in the ANPR. Again, preparation of a grid would help identify the concerns which must be addressed and aid the evaluation of the pros and cons of the alternative solutions.

Some of the questions which need to be addressed are:

- Who would set the tax or control the permits?
- What would be the control mechanism? What records and auditing would be required?
- When would levels be set? How would they be phased in? How far in advance and for what duration would levels be set for?
- What notification procedure would precede auctions or changes in the levels of permits or taxes?

Economic Incentives Options

- If permits were selected, what recourse would be available to those missing the allocation or auction, or for new entries?

c. Legal Issues (Also See Section III)

i. Taxes

It is clear that administrative agencies have no constitutional authority to levy a tax. Any effort by the EPA to impose a tax could be met with a successful constitutional attack. Thus, if EPA decides a tax is the preferred method of regulating CFCs, it will be necessary to go to Congress to secure passage of a tax bill.

ii. Marketable Permits

The Rand Report and EPA in the ANPR set forth two alternatives for distributing CFC permits. The first involves EPA setting the total CFC emissions limit, and then granting permits based on users' percentage of the total emissions prior to EPA limitation. The second is to sell the permits at an auction. There are different legal concerns with respect to the two alternatives:

- Allocation - This would require EPA to determine each user's relative market share and then grant permits accordingly. Aside from the antitrust implications of using market share, and the natural reluctance of firms to release such sensitive information, it is difficult to see how EPA could reconcile the share numbers, without accusations and perhaps challenges of unfairness.

Economic Incentives Options

- Auction - It is possible that if EPA chose to impose an auction system to control CFC production, the Agency would be vulnerable to challenge on the grounds that the system was in effect a "tax" on the production of CFCs. As noted earlier, EPA does not have the authority to impose a tax.

Regardless of which implementation system were selected or the associated legal questions, serious problems emerge from the legal ramifications of how a marketable permit system would operate in practice.

The Rand Report and EPA discuss the possibility of futures markets developing for permits, or sales of permits through a national securities exchange or through a commodities market, and of Federal regulation of such markets. The more sophisticated the trading in permits becomes, the more likely it is that Federal securities laws will become involved. The precise nature of this involvement, and the impact the interaction between Federal securities and environmental laws will have on the system, is a complex issue and requires further examination.

Lastly, the Rand Report states that collusion among firms and predatory behavior in the permit marketplace will not be unacceptable because neither would diminish the emission-reducing potential of a permit policy. Nevertheless, this potential must be examined in depth because of antitrust questions. A marketable permit system such as proposed by Rand could be noncompetitive in nature. The pro-competitive policies of the antitrust laws are important national objectives that cannot reasonably be ignored by EPA. The impact to the proposed permit system could be contrary to the policy objectives of the antitrust laws.

X. APPENDIX J

CHLOROFLUOROCARBON
PRODUCTION AND EMISSIONS

CFC PRODUCTION AND EMISSIONS

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1. INTRODUCTION

Two of the Agency's stated major justifications for a decision to regulate now are that: 1) world production and use of CFCs have essentially offset the reduction created by the U.S. aerosol use ban, and 2) estimates of future growth in world production and use make the potential problem of ozone depletion even more severe than the cited model calculations, because these calculations are based on an assumption of constant emissions at 1977 rates. Thus, careful examination of the Agency's production and use estimates, both current and for future years, is of great importance to the underlying question of risk and the need for immediate regulation.

In the ensuing analysis and discussion we find the Agency's estimates in the ANPR to be inconsistent with available data and illogical opposite recent and projected trends. This is particularly disconcerting in light of our efforts [Du Pont, 1978; Masten, 1980] to provide thorough and accurate data to the Agency and its contractors in hopes that such cooperation would result in a reliable, shared data base on which deliberations and decisions could be made.

It should be noted that a meaningful discussion of EPA's treatment of current and projected production and emission figures for CFCs in the U.S. and the world is difficult due to the irreproducibility of EPA's numbers. The sources referenced in the ANPR offer either no numbers or substantially different numbers than those used by EPA for the categories discussed.¹

¹ The Agency issued a memo from Carroll Bastion to E. Douglas Kenna on 12/11/80 which contained analyses of how EPA reached some of its estimates, and which acknowledged numerous errors in previously cited estimates. Receipt of this memo on 12/15/80 did not permit incorporation of analysis of its contents in Du Pont's ANPR response. It will be responded to at a later date, and this response should be considered part of Du Pont's ANPR comments.

CFC Production and Emissions

2. CURRENT U.S. CFC PRODUCTION

In the ANPR, it is stated:

"Production of CFCs in the United States is expected to grow at a 7 percent annual rate [in the absence of any further regulation] from 600 million pounds in 1980 to 1.2 billion pounds in 1990, according to the report on CFC control written for EPA by the Rand Corporation."

The cited Rand Report provides the following estimates for CFC production of CFC-11, 12, 22 and 113 (quantities in 10^6 lb.):

	1976 [Rand, 1980, Table 3.1]		1990 [Rand, 1980, Table 3.3]	
	<u>Total</u>	<u>Total Minus CFC-22</u>	<u>Total</u>	<u>Total Minus CFC-22</u>
Production	891	721	1147	762
Sales for Non-aerosol use*	474	357	957	692

*A term defined as production minus aerosol use and "minus internal use, exports, packaging and transport emissions, and certain limited refrigeration uses."

The first thing to be noted is that Rand makes no estimates for 1980. Second, the estimates Rand does make (1976) include the use of CFC-22 as an intermediate which, because it is a non-emitting use, should be subtracted from all production and emissions estimates.

CFC Production and Emissions

Actual production of the five major CFCs² in 1980 is estimated by Du Pont to be approximately 755 million pounds, excluding CFC-22 used as an intermediate.³ Over the last three years Du Pont annually has analyzed data published by the United States International Trade Commission for CFCs-11, 12 and 22, and supplemented these data with Du Pont's estimates of CFC-113 and 114 production. Table 1 below shows production for the years 1977, 1978 and 1979 by product and by total.

TABLE 1

U.S. CFC PRODUCTION
(10⁶ LB.)

<u>Year</u>	<u>CFC-11</u>	<u>CFC-12</u>	<u>CFC-22</u>	<u>CFC-113</u>	<u>CFC-114</u>	<u>TOTAL</u>
1977	213	358	134	100	25	830
1978	194	327	156	100	29	806
1979	173	287	153	124	18	755

It is quite obvious from this data and preliminary estimates for 1980 sales, that production of the five major CFCs in 1980 will substantially exceed the 600 million pound figure put forth by EPA.

²CFC-11, 12, 22, 113 and 114.

³All production figures for CFC-22 in this Appendix exclude CFC-22 use as an intermediate. We estimate this use in 1979 was approximately 60 million pounds. Therefore, total CFC production in 1979 was approximately 815 million pounds. This figure was used in Section II-CFC Uses and Essentiality - as the basis for calculating the approximate percentages of total CFC production by end use application.

3. PROJECTED GROWTH OF U.S. CFC PRODUCTION

EPA's projection that U.S. CFC production will reach 1.2 billion pounds by 1990 seems questionable. Rand did estimate 1990 U.S. production at 1147 million pounds, but this must be put into context. As noted in the previous section, the estimate is overstated because it includes CFC-22 production which is used as an intermediate, a non-emitting use. Additionally, the situation at the time of Rand's work (1978-1979) and the underlying assumptions made by Rand at that time are quite different than today's realities.

Rand assumed in its base case that there would be no further regulations and, implicitly, no threat of further regulation. In reality, of course, the threat of regulation of the non-aerosol uses of CFCs has been keenly felt over the last few years and EPA's pronouncements over the past year have only intensified this concern. Regardless of the level of regulatory activity on CFCs by EPA, until such time as the validity of the depletion theory is resolved, CFC-users will continue to be highly uncertain over the future for CFCs. Such concern will have a dampening effect on future growth -- users will be reluctant to commit to new products or processes dependent upon an unsure future availability of CFCs. Only a favorable resolution of the theory, with an attendant removal of any future regulatory threat would result in actual growth approaching Rand's projections.

This uncertainty also affects the CFC producers to a degree which further throws into question the appropriateness of EPA using Rand's artificial base line estimate as a real world forecast. Under the base line numbers, substantial production capacity would have to be added for the U.S. production to reach 1.2 billion pounds of CFCs. But it is highly improbable that

CFC Production and Emissions

business managers would make the significant capital investments required to build new capacity (generally about \$0.85 per pound of annual capacity) due to the great uncertainty whether such expansion could return its investment in the face of possible further major CFC regulation. We are aware of no indications that substantial additional CFC capacity has been initiated or planned.

The combination of erroneous base figures for 1980 CFC production, coupled with an unrealistic estimate of 1990 production given the current regulatory climate, makes the 7 percent growth rate projected by EPA unreasonable and unsupportable.

4. WORLD CFC EMISSIONS AND GROWTH

EPA states in the ANPR:

"Total world emissions, in the absence of any further regulation, are projected to grow at a 9 percent annual rate over the next decade, from 1.5 billion pounds in 1980 to 4.5 billion pounds in 1990, according to EPA analysis of data collected for the Chemical Manufacturers Association."

There are several problems with this statement:

a) First, these numbers represent another example of EPA's careless treatment and publication of numbers. If one assumes that 1980 world emissions will total 1.5 billion pounds and then projects a 9 percent annual growth for 10 years, the result is 3.55 billion pounds, not 4.5 billion pounds.
[$1.5 \times (1.09)^{10} = 3.55$]

b) Second, EPA alludes to an analysis of data provided by the Chemical Manufacturers Association (CMA) to lend credence to their figures. Table 2 on the next page shows the CMA data [CMA, 1980b] for the years 1974-1979 for CFC-11 and 12, the only CFCs consistently reported on by CMA.

CFC Production and Emissions

TABLE 2

CHEMICAL MANUFACTURERS' ASSOCIATION
WORLD PRODUCTION OF CFCs-11 and -12
(10⁶ LB.)

<u>YEAR</u>	<u>CFC-11</u>	<u>CFC-12</u>	<u>TOTAL</u>
1974	833	1045	1878
1975	714	923	1637
1976	772	992	1764
1977	732	936	1668
1978	708	913	1621
1979	666	882	1548

Compound Annual Rate: -3.8 percent

Du Pont's estimate of world production of the five major CFCs is shown below in Table 3.

TABLE 3

WORLD CFC PRODUCTION

(10⁶ LB.)

<u>YEAR</u>	<u>CFC-11</u>	<u>CFC-12</u>	<u>CFC-22</u>	<u>CFC-113</u>	<u>CFC-114</u>	<u>TOTAL</u>
1977	732	936	226	155	40	2089
1978	708	913	252	175	47	2095
1979	666	882	289	201	40	2078

Compound Annual Rate: -0.26 percent

CFC Production and Emissions

It is difficult, if not impossible, to understand how EPA could interpret the available data, which shows a declining trend for world production, as supporting their claim of a 9 percent growth rate for the next decade.

c) Third, the European Economic Community (EEC) has recently called for a 30 percent reduction of CFC use in aerosols from 1976 levels by December 1981. EPA states in the ANPR that EEC members accounted for 39 percent of the world production of CFCs in 1977. Therefore, it seems even more unlikely that world growth could approach the 9 percent level claimed by EPA.

d) Fourth, similar to the U.S. situation, such growth of world CFC production would require major capacity additions, which, in turn, would require major new capital investments in manufacturing facilities. Although other countries have not taken the severe actions being pursued by EPA, bans or mandated reductions in aerosol use of CFCs by some nations, coupled with an EEC moratorium on new capacity for CFC-11 and 12, have generated sufficient concern to make investments in major new capacity prior to resolution of the science improbable.

5. U.S. SHARE OF WORLD CFC PRODUCTION

In 1971, the U.S. share of world production of CFCs was about 51.5 percent [IMOS, 1975]. Since that time, U.S. share has steadily declined. Table 4 below (Du Pont estimates) compares the U.S. production of CFCs to the world total, illustrating the ongoing decline in U.S. share.

TABLE 4

U.S. SHARE OF WORLD CFC PRODUCTION

CFCs-11, 12, 22, 113, 114

(10⁶ LB.)

<u>YEAR</u>	<u>WORLD PRODUCTION</u>	<u>U.S. PRODUCTION</u>	<u>U.S. SHARE (%)</u>
1977	2089	830	39.7
1978	2095	806	38.5
1979	2078	775	36.3

As discussed in detail in Section VI, further regulation of U.S. production and use alone cannot solve the problem, if it exists. In the ANPR, EPA's Table 3 graphically illustrates that further unilateral action by the U.S. does not significantly alter the total ozone depletion potential.

6. ESTIMATES SHOULD BE BASED ON CALCULATED OZONE DEPLETION
POTENTIAL FACTORS - PERMIT POUNDS, NOT CFC POUNDS

In the ANPR, EPA discusses the depletion potential factors for the different CFCs. (We provide our updated methodology and results in Appendix G.) However, no effort has been made by EPA to integrate this important concept into the discussions of CFC production and emission growth. Table 5 shows the U.S. production of major CFCs for several recent years adjusted for calculated ozone depletion potential. It is significant that actual pounds have decreased at an annual rate of roughly 5 percent but the rate of decline has been roughly 7.0 percent when the data is adjusted for the calculated relative depletion potential.

Comparable analysis of the world production of CFCs is shown in Table 6. The actual world pounds have declined at an annual rate of roughly 0.3 percent but the relative depletion potential adjusted pounds have declined at an annual rate of approximately 2.1 percent.

TABLE 5

U.S. CFC PRODUCTION (10^6 Lbs.)
ADJUSTED FOR CALCULATED RELATIVE OZONE DEPLETION POTENTIAL

(Normalized for CFC-11 = 1.0)

CFC #	1977			1978			1979		
	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.
CFC-11	213	1.00	213	194	1.00	194	173	1.00	173
CFC-12	358	0.84	301	327	0.84	275	287	0.84	241
CFC-22 ⁴	134	0.03	4	156	0.03	5	153	0.03	5
CFC-113	100	0.82	82	100	0.82	82	124	0.82	102
CFC-114	25	0.61	15	29	0.61	18	18	0.61	11
TOTAL	830		615	806		574	755		532

Approximate Annual Growth Rates:

- Actual Pounds ~-5 percent
- Calculated Ozone
Depletion Potential
Adjusted Pounds ~- 7 percent

⁴Excluding CFC-22 used as Intermediate

TABLE 6

WORLD CFC PRODUCTION (10^6 Lbs.)
ADJUSTED FOR CALCULATED RELATIVE OZONE DEPLETION POTENTIAL

(Normalized for CFC-11 = 1.0)

CFC	1977			1978			1979		
#	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.	Actual Lbs.	Calculated Relative Depletion Potential	Adjusted Lbs.
CFC-11	732	1.00	732	708	1.00	708	666	1.00	666
CFC-12	936	0.84	786	913	0.84	767	882	0.84	741
CFC-22 ⁵	226	0.03	7	252	0.03	8	289	0.03	9
CFC-113	155	0.82	127	175	0.82	144	201	0.82	165
CFC-114	40	0.61	24	47	0.61	29	40	0.61	24
TOTAL	2089		1676	2095		1656	2078		1605

Approximate Annual Growth Rates:

- Actual Pounds ~- .3 percent
- Calculated Ozone
Depletion Potential
Adjusted Pounds ~- 2.1 percent

⁵Excluding CFC-22 used as Intermediate

CFC Production and Emissions

Clearly, a production decrease of the CFCs of higher calculated ozone depletion potential results in the total ozone depletion potential adjusted pounds declining more sharply than the decline in actual pounds. The regulatory initiatives elsewhere in the world are focusing on CFC-11 and CFC-12 (the very compounds with the greatest calculated potential for ozone depletion) as aerosol propellants (e.g., the EEC 30 percent cutback). Therefore, actual future production of CFCs should continue to overstate the potential for calculated future ozone depletion. This important fact must be considered by EPA when projecting future production and emission figures, since any ozone depletion occurring will be proportional to the ozone depletion potential adjusted pounds, not the actual pounds of production or emissions. EPA should not use one set of numbers (ozone depletion potential pounds or permit pounds) to make its case in one argument but switch to a second set (actual pounds) to make its case in another.

7. SUMMARY

In summary, EPA's analysis of production and emissions is inaccurate, misleading and unsubstantiated. The above comments show that:

- 1980 U.S. CFC production (excluding CFC-22 used as an intermediate) will approach 755 million pounds, not 600 million pounds.
- It is very improbable that U.S. CFC production would grow at 7 percent through 1990.
- It is unreasonable to project a 9 percent growth rate for world CFC emissions.
- U.S. share of CFC production has been declining.
- The calculated potential for ozone depletion must be considered when analyzing and projecting the production and emissions of CFCs.

X. APPENDIX K

INDUSTRY FUNDED FLUOROCARBON RESEARCH PROGRAM -
EFFECT OF CHLOROFLUOROCARBONS ON THE ATMOSPHERE

(PREPARED BY CHEMICAL MANUFACTURERS ASSOCIATION -
FLUOROCARBON PROJECT PANEL)

Note: References cited in Appendix K are internal to this appendix and are not necessarily listed in Section XI "BIBLIOGRAPHY."



CHEMICAL MANUFACTURERS ASSOCIATION

Fluorocarbon Research Program

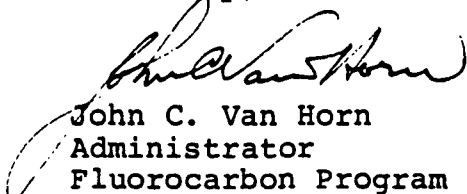
Effect of Chlorofluorocarbons on the Atmosphere

Revision No. 14

The Fluorocarbon Research Program, sponsored and funded by the industry is summarized in Revision No. 14, November 30, 1980. *Italics* indicate developments since Revision No. 13.

For additional information, please contact the investigator or CMA. Please note the new CMA address.

Sincerely,



John C. Van Horn
Administrator
Fluorocarbon Program
Telephone: 202/887-1194

Attachment: Revision No. 14
November 30, 1980

K-ii

SUMMARY

Research Program on

EFFECT OF CHLOROFLUOROCARBONS ON THE ATMOSPHERE

Sponsored by: The Chlorofluorocarbon Industry

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(Originally Issued: September 26, 1975)

Revision No. 14: November 30, 1980

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SUMMARY

Research Program on

EFFECT OF CHLOROFLUOROCARBONS ON THE ATMOSPHERE

Sponsored by the Chlorofluorocarbon Industry

Administered by the Chemical Manufacturers Association

(Originally Issued: September 26, 1975)

Revision No. 14: November 30, 1980

This summary describes work supported by the manufacturers of chlorofluorocarbons (CFCs, sometimes called fluorocarbons) in an attempt to assess the possible impact of these chemicals on the environment and, in particular, on the stratospheric ozone layer.

Summary and Recommendations

In 1972 the CFC manufacturers began supporting a program to investigate the effects of CFCs on the environment. This program has been expanded greatly to help determine the extent, if any, to which these compounds may affect the stratospheric ozone layer. Industry and government-sponsored scientists working on the halogen-ozone problem have cooperated effectively. Continuation of this cooperation ~~is~~ essential, with special attention to providing periodically updated summaries of research priorities, programs, and results, together with critical analyses of the reliability and significance of the data.

The programs now under way to develop methods for determining the ozone changes that are actually occurring (as opposed to hypothetical or calculated ozone changes), to determine the actual tropospheric lifetimes of CFCs 11 and 12 (now assumed to

be infinite in most models), and to resolve important questions about key stratospheric species-- O_3 , ClO , total chlorine--will lead to a much better understanding of the effect of the CFCs on stratospheric ozone.

The industry position continues to be:

- . The ozone depletion theory warrants serious concern and continuing investigation.
- . The international scientific consensus necessary to resolve this issue must be based on convincing measurements and evaluations, not theory.
- . Convincing experimental evidence can be obtained to verify or disprove the theory quantitatively.
- . There is time to perform these necessary experiments without significant risk to the health and welfare of the population.

The Industry-Sponsored Program

In July of 1972, E. I. du Pont de Nemours & Company issued to CFC manufacturers worldwide an invitation to a "Seminar on the Ecology of Fluorocarbons." Its purpose was to establish a technical program because, as stated in the invitation,

"Fluorocarbons are intentionally or accidentally vented to the atmosphere worldwide at a rate approaching one billion pounds per year. These compounds may be either accumulating in the atmosphere or returning to the surface, land or sea, in the pure form or as decomposition products. Under any of these alternatives, it is prudent that we investigate any effects which the compounds may produce on plants or animals now or in the future."

Representatives of 15 companies attended the meeting, agreed that such a program was important, and established and funded a CFC research program under the administration of the Chemical Manufacturers Association (CMA). Thus, in 1972, with no evidence that CFCs could harm the environment, the producers of these chemicals agreed that there was a need for more information and proceeded to act.

The CFC producers supporting this program (see Table 1, p. 10) represent almost the total free world production of CFCs. The research is directed by the CMA Fluorocarbon Project Panel with one member from each supporting company. This Panel meets regularly to review progress on current research, evaluate new proposals, and exchange data with contractors, with government agencies, and with other scientists. A significant fraction of the support for this program comes from European CFC producers, and two meetings per year are held in Europe.

Publication of the Rowland-Molina hypothesis in 1974 identified a potentially serious problem, so the CMA research program was expanded considerably. The CFC-ozone relationship attracted the attention of many scientists in academic and government laboratories, legislative and regulatory bodies, and the press. CMA's program is concentrating on research most likely to answer the critical question: to what extent will CFCs affect the stratospheric ozone layer?

To strengthen the overall effort to find the answer, CMA has attempted to coordinate its efforts with others working on the same or related problems such as the Supersonic Transport and the space shuttle. All of these problems concern the federal government, and interactions with a number of agencies have been especially helpful in:

1. Taking advantage of the knowledge and experience gained in the Climatic Impact Assessment Program;
2. Coordinating funding of programs addressing the halogen-ozone problem;
3. Planning joint experiments with government research groups; and

4. Helping to set priorities for industry-sponsored research.

About 355 research proposals have been reviewed to date, and projects totaling about \$9.5 million have been funded (see Table 2, p. 11). Calendar 1981 commitments are expected to be *almost* \$2 million, and total expenditures through 1981 will be over \$11 million.

Assessment of Uncertainties

Two groups in the United States were charged during 1975 with looking exclusively at the scientific aspects of the halo-carbon-ozone problem and making recommendations for further work. In May 1975 the government's Interdepartmental Committee for Atmospheric Sciences (ICAS) made recommendations for research and monitoring programs. In July 1975 the Panel on Atmospheric Chemistry of the National Academy of Sciences (NAS) identified a number of areas in which relevant data are nonexistent, fragmentary, or insufficient and in September 1976 issued a final report containing recommendations for pertinent studies. Its parent committee, the NAS Committee on Impacts of Stratospheric Change, then recommended that up to two years be allowed before a decision was made on the necessity for restrictive action.

The Clean Air Act Amendments of 1977 (U. S. Public Law 95-95) established the U. S. Environmental Protection Agency (EPA) as the agency responsible for assessing the probable effect of CFCs on the ozone layer. Other U. S. agencies are given various responsibilities in the scientific effort required to support any decisions, and the EPA is required to rely on the NAS for advice on the status of the science. In November 1979 the NAS Panel on Atmospheric Chemistry and Transport issued its latest report on the status of the CFC-Ozone theory.

Significant additions to pp. 4 - 9 since the last revision are *italicized*.

Goals of the Industry-Sponsored Program

The emphasis of the CMA-administered industry program has been overwhelmingly in the major areas recommended for further study by the NAS Panel and ICAS. The industry-sponsored program, therefore, aims to fill in the most important gaps in existing scientific knowledge. The only major area not in the CMA program is acceleration of ozone monitoring, which can be accomplished more appropriately by governmental and international agencies. In addition, the CMA program has included work to correlate UV radiation reaching the ground with ozone measurements and to improve the statistical treatment of ozone data so that very small abnormal changes can be detected in a much shorter period of time than was previously believed possible.

The current CMA research program is consistent with the needs and tasks identified recently by the NAS*:

- . Specific tasks include measurement of the wavelength dependent quantum yields [photochemical reaction rates] and branching ratios [distribution between alternative reaction products] of the stratospheric photolysis of species such as O_3 , $ClONO_2$, $HOCl$, and NO_3 . [Page 45].
- . [Studies of] stratospheric chemical processes [such as] those with negative activation energies and incomprehensible A factors [currently unexplainable differences between theoretically and experimentally derived mathematical expressions for the reaction rates]. Reactions of HO_2 species are a particular, but not the only, example of this need. [Page 45].

*Panel on Stratospheric Chemistry and Transport, Committee on Impacts of Stratospheric Change, National Research Council, "Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport", National Academy of Sciences, Washington, D. C., November, 1979. Added material is identified by square brackets [], as are the pages in the reference where the needs and tasks appear.

- . Laboratory studies of the decomposition of [CFCs] on desert sand should be designed to provide data from which atmospheric lifetimes could be directly calculated. [Page 72].
- . In several cases, simultaneous measurements of photochemically related species (and perhaps solar flux) are needed, ... [Page 100].
- . In particular, in the case of the anthropogenic halocarbon compounds, the global spatial concentration distribution and the temporal increase need to be better determined. F-11, F-12, and CH_3CCl_3 are especially important. More F-21 measurements should be carried out. [Pages 133, 134].
- . A total chlorine concentration measurement would be of great value. [Page 134].
- . Reduction of these ranges of uncertainty will require more sophisticated and carefully analyzed 2-D and, ideally, 3-D models [Page 169].

The current CMA program also is consistent with the June 1978 recommendation of the Royal Society Study Group,* which summarized their position as:

"The surface release of chlorofluoromethanes was considered to be a potential, but so far unverified, long-term hazard which requires considerable further research. Particular attention must be paid to:

- (a) the investigation of possible tropospheric sink processes, since these can have a major effect on predicted effects on stratospheric ozone,

*Royal Society Study Group, Final Report, June 28, 1978, "Pollution in the Atmosphere - V. Problem Areas: Scientific Priorities for Research."

- (b) the simultaneous measurement of key reactants, transient intermediates and products in the stratosphere in order to test the model hypothesis and to direct future research, and
- (c) the development of 2- and 3-dimensional models to represent more realistically motions in the atmosphere.

It was agreed that there is no need for hasty action and that 3-4 years can be allowed for the research programmes currently in train to produce their results."

Efforts to Resolve Current Uncertainties

There are presently several discrepancies and/or uncertainties that the CMA program is trying to resolve. Its stratospheric measurement program includes the collection of more data on total Cl, ClO, and HCl to determine the correctness of current indications that their concentrations do not fit predicted profiles. The observation by others that high ClO concentrations unexpectedly coexist with normal odd oxygen levels emphasizes the need for more information on the concentration of chlorine species. Simultaneous measurement of several species is necessary to provide a rigorous test of the models, so the stratospheric measurement program is also aimed at simultaneous measurement of important chemical species that are known or believed to be present in the stratosphere.

In addition to in situ stratospheric measurements during balloon flights, the CMA program includes an effort to develop ground-based monitoring techniques for some of the important atmospheric species. HCl and HF now are routinely measured from the ground at Jungfraujoch in Switzerland. Although a ground-based method to monitor ClO has been developed, its sensitivity is as yet insufficient for accurate measurement of ClO. This program is continuing, and it is expected that the sensitivity of the method will be increased by about a factor of 7 during 1980, permitting accurate, ground-based measurements of this important stratospheric species.

Another goal of the CMA program is to determine the tropospheric lifetimes of certain CFCs. In 1977 the CMA initiated a program to determine the tropospheric lifetimes of selected compounds. Five stations have been set up, three in the northern hemisphere (Lovelock and Simmonds, Rasmussen) and two in the southern (Rasmussen), to measure the concentrations of CFCs 11 and 12 and other important species several times a day. Workup of the analytical data, including incorporation of data on meteorological conditions at each site, is being carried out under the direction of CMA modeling contractors (Cunnold, Alyea, Prinn). This program may require a period of three or more years to yield definitive results.

The CMA program also seeks to measure rates for those reactions for which the rates are not well established, measure the ultraviolet and infrared spectra of compounds that may be present in the stratosphere, and search for chemistry that has not yet been included in present atmospheric models. Measurements made thus far have demonstrated the significance of ClONO_2 , which was not originally included in stratospheric models, and have pointed to the probable importance of HOCl in stratospheric chemistry. The program also funds general studies of HO_2 chemistry, which led to the revision of the rate constant for the reaction of HO_2 with NO and essentially eliminated nitrogen oxides as suspected ozone depleters. Another study in progress is the investigation of the formation of higher chlorine oxides.

Model evaluation and improvement is another facet of the CMA program. One objective is to determine to what extent computer models represent the "real world", and a second is to improve models in such matters as the diurnal nature of solar radiation and extension to two-dimensions. One value of two-dimensional models is that they permit description of atmospheric species in terms of both altitude and latitude and include seasonal variations, facilitating comparison with measurements at a given location.

Statistical time series analysis is being used to detect trends in ozone data that are small compared to observed natural

variations. The method appears very sensitive and may be capable of establishing a small ozone depletion over a long period of time. The depletion calculated to date is larger than the detection threshold as determined solely on a statistical basis, but the extent to which other factors increase the threshold is still uncertain. Ground-based and satellite data are being analyzed for trends, and methods to assess the magnitude of long-term natural trends and instrument drift are being investigated. This approach is especially attractive because it seeks to answer directly the question of prime importance: is stratospheric ozone depletion really occurring to the extent predicted by the models?

More detail on the CMA program is given in Tables 3, 4A, and 4B. Table 3 (p. 12) lists summaries of the projects by type of research activity. Table 4A (p. 44) lists completed projects, and Table 4B (p. 53) lists active projects in chronological order of funding. Table 5 (p. 57) lists publications resulting from industry-sponsored work. A document that relates the goals of the individual industry-sponsored projects to the reduction of uncertainties in the CFC-ozone question has been submitted to EPA.*

In addition to the work supported by the CFC industry at universities and other laboratories, there are studies underway in the laboratories of individual member companies who have scientists able to make significant contributions to the resolution of the problem. Three problems have received particular attention by industry scientists: the identification and quantification of tropospheric sinks for CFCs, the application of statistical methods to detect abnormal trends in stratospheric ozone concentrations, and the evaluation and development of modeling techniques.

*The Fluorocarbon Industry Research Program and Current Uncertainties in the Ozone Depletion Theory, E. I. du Pont de Nemours & Company, Inc., November, 1979.

Table 1
CHLOROFLUOROCARBON MANUFACTURERS
represented on the
CMA TECHNICAL PANEL ON CHLOROFLUOROCARBON RESEARCH

Akzo Chemie bv (Holland)
Allied Chemical Corporation (U.S.)
Asahi Glass Co., Ltd. (Japan)
Australian Fluorine Chemicals Pty. Ltd. (Australia)
Daikin Kogyo Co., Ltd. (Japan)
E. I. du Pont de Nemours & Company, Inc. (U.S.)
Essex Chemical Corporation (Racon) (U.S.)
Du Pont Canada, Inc. (Canada)
Hoechst AG (West Germany)
Imperial Chemical Industries Limited (England)
I.S.C. Chemicals Ltd. (England)
Kaiser Aluminum & Chemical Corporation (U.S.)
Kali-Chemie Aktiengesellschaft (West Germany)
Mitsui Fluorochemicals Co. Ltd. (Japan)
Montedison S.p.A. (Italy)
Pennwalt Corporation (U.S.)
Rhône-Poulenc Industries (France)
Showa Denko K. K. (Japan)
Ugine Kuhlmann, Produits Chimiques (France)
Union Carbide Corporation (U.S.)*

November 30, 1980

*Does not currently manufacture chlorofluorocarbons.
Supported the CMA program through June, 1977.

Table 2

CHLOROFLUOROCARBON RESEARCH PROGRAM

Administered by
Chemical Manufacturers Association

Financial Summary

Type of Activity ^a	Completed Projects	Active Projects	Total
A. Reaction Rate Constant Measure- ments	\$ 494,016	\$ 409,507	\$ 903,523
B. Source and Sink Studies	1,297,343	410,091	1,707,434
C. Laboratory Studies Related to Potential Atmospheric Measurements	693,796	427,347	1,121,143
D. Tropospheric and Stratospheric Measurements	1,825,967	1,249,906	3,075,873
E and F. Modeling and Other Projects	1,033,082	978,594	2,011,676
G. Consulting	140,403	42,869	183,272
	-----	-----	-----
SUBTOTAL	\$5,484,607	\$ 3,518,314	\$ 9,002,921
Administrative Expenses			509,714

TOTAL			\$ 9,512,635

^aIndividual projects are summarized in Table 4.

November 30, 1980

Table 3*

Chlorofluorocarbon Research Program

Types of Research Activities, Summaries

A. Reaction Rate Constant Measurements

Dr. J. W. BIRKS -- University of Illinois -- 75-1, 76-117A. Measurement of Reaction Rates Relevant to the Fluorocarbon-Ozone Problem (completed).

Reaction rates were measured at various temperatures by a discharge flow technique, and a quadrupole mass spectrometer was used for detection of products. The reaction $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$ has the reaction rate $4.40 \pm 0.66 \times 10^{-33} \exp[(1087 \pm 70)/T] \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ for $\text{M} = \text{N}_2$. No reaction of ClONO_2 with NO , NO_2 , O_3 , or HCl was observed, indicating that these reactions are unimportant as sinks for ClONO_2 .

Reaction rates for $\text{ClO} + \text{O}_3 \rightarrow \text{OClO} + \text{O}_2$, $\text{ClO} + \text{O}_3 \rightarrow \text{ClOO} + \text{O}_2$, and $\text{OClO} + \text{O}_3 \rightarrow \text{ClO}_3 + \text{O}_2$ rule out successive oxidation of chlorine to perchloric acid based on the calculated photolysis constant for OClO of $7.6 \times 10^{-2} \text{ s}^{-1}$, but there is currently disagreement on the accuracy of the calculated photolysis constant.

The reaction $\text{ClO} + \text{H}_2\text{O}_2$ was not rapid enough to measure, with no evidence for new products. The reaction $\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$ has a reaction rate between 10^{-13} and $10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The reaction $\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{O}_2$ (primarily, $\rightarrow \text{HO} + \text{ClO}$ to a minor extent) is fast. The reaction $\text{ClO} + \text{SO}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{ClOO} + \text{SO}_3$ is slow.

Rate measurements on $\text{NO} + \text{O}_3$, $\text{O} + \text{ClONO}_2$, and $\text{BrO} + \text{NO}_2$ have been studied. A 15% higher activation energy for $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ has been measured. Four-center reactions of ClOCl with Cl , O , N , or ClO were studied by molecular beam mass spectrometry, with reaction at the O atom in ClOCl indicated in each case.

Dr. J. W. BIRKS -- University of Colorado -- 77-192, 78-244, 79-276, 80-321, 80-329. Studies of Homogeneous and Heterogeneous Reactions of Importance in the Stratosphere.

The studies that were made at the University of Illinois (75-1 and 76-117A, p. 12, and 76-117B, p. 17) are being continued.

*Significant additions since the last revision are *italicized*.

Table 3 (continued)

The rate constant for the reaction $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ was found to be independent of pressure over the range 2-6 torr, the result being $k_1 = (4.5 \pm 0.9) \times 10^{-12} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$. An upper limit of 2% for the branching ratio to the alternative products of this reaction, $\text{HCl} + \text{O}_3$, was established by attempting to detect ozone as a reaction product. The effect of O_2 or N_2 in the presence of He or Ar on the ClO^+ mass spectrometer ion current at room temperature and at 245°K is also being studied. A value for the reaction rate for $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ has been obtained, agreeing with previous measurements (3 to 4 $\times 10^{-12} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$). The temperature dependence will be examined.

The rate constants for the reaction of HO with HOCl and with HO_2NO_2 will be measured using a flash photolysis-resonance fluorescence technique. A quadrupole mass spectrometer operating in the positive ion mode will be used for detection in these reactions. The technique of negative ion mass spectrometry will be developed for determining products and measuring the rate constants for the following reactions: $\text{HO} + \text{HO}_2$, $\text{ClO} + \text{HO}_2$, $\text{ClOO} + \text{NO}$, and $\text{OClOO} + \text{NO}$. In addition the flash photolysis products from HOCl, ClOO, and OClOO are to be examined. The nature of these products and the quantum efficiency with which these species photolyze are potentially important factors in the calculation of the ozone depletion estimate in the presence of odd chlorine.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 76-100. Laser Magnetic Resonance Study of HO_2 Chemistry (completed).

HO_2 reactions of stratospheric importance are being measured using a laser magnetic resonance technique. The rate constant for the reaction $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HOONO}_2 + \text{M}$ is 1.5 to $2.0 \times 10^{-31} \text{ cm}^6\text{molec}^{-2}\text{s}^{-1}$. The major pathway is the production of peroxyntitric acid, a species not previously considered in the models.

The rate constant for the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$ is $8 \pm 2 \times 10^{-12} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$ at room temperature, a value about 30 times faster than the previously accepted value. The temperature dependence of this reaction has been measured.

The rate constant for the reaction between HO_2 and O_3 is $1.4 \times 10^{-14} \exp(-580/T) \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$.

The reactions of HO and HO_2 with N_2O_5 appear to be very slow and consequently not important in the atmosphere.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder - 77-223. Study of ClO Chemistry by Laser Magnetic Resonance (completed).

The rate constant for the reaction $\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$ is $3.3 \times 10^{-11} \exp(-850/T) + 4.5 \times 10^{-12}(T/300)^{-3.7} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$

Table 3 (continued)

over the temperature range 235-393°K. Thus the reaction has a negative activation energy, indicating the possibility of an intermediate complex. A search is in progress for O_3 , a product of the alternate channel $HO_2 + ClO \rightarrow HCl + O_3$, which would act as an odd oxygen source (cf. 79-289, p. 14).

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 79-289. Kinetic Studies of Stratospheric Chlorine Chemistry.

A system suitable for determining the products of many significant atmospheric reactions using tunable infrared diode laser detection has been built.

A new method for accurately measuring N_2O in the atmosphere using a tunable diode laser has been developed. A flow system using LMR detection has been built for measuring the rate constants of important reactions at pressures and temperatures corresponding to those actually present in the stratosphere.

Dr. M. J. KURYLO -- National Bureau of Standards -- 78-233. Rates of Reaction of Cl Atoms with the Primary Products of Alkane Photooxidation (completed).

Flash photolysis resonance fluorescence (FPRF) has been used to establish an upper limit rate constant for $Cl + OCS$ ($1 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (220-323°K)). The reaction rate for $Cl + H_2CO$ has been confirmed as $(1.09 \pm 0.4) \times 10^{-10} \exp[-(131 \pm 98)/T] \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. The rate for $OH + CH_3CCl_3$ is $(5.41 \pm 1.84) \times 10^{-12} \exp[-(1813 \pm 95)/T] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. This lower rate suggests higher tropospheric OH concentration. An upper limit of $< 3 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for the reaction $CH_3 + O_2 \rightarrow OH + H_2CO$ at 368°K is based on failure to detect either product.

The temperature-dependent rate for the ozone formation reaction $O + O_2 + M$ ($M = N_2, O_2, Ar$) has been measured, providing the first detailed analysis for $M = N_2$ and O_2 , and indicating a weaker temperature dependence than previously assumed for O_2 . The recommended value for ozone formation in air [$1.07 \times 10^{-35} \exp(525 \pm 60/T) \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$] is similar to the current NASA recommendation. Studies of atmospheric quenching of $O_2(^1\Delta, V > 0)$ indicate that vibrational quenching dominates over any possible reactivity of this species in the stratosphere.

Dr. M. J. KURYLO -- National Bureau of Standards -- 80-307. Reactions within the HO_x Cycle.

Flash photolysis resonance fluorescence will be used to measure rate constants for the reactions $HO_2 + HO_2$, $HO + HO_2NO_2$, and $HO + H_2O_2$.

Table 3 (continued)

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 74-2. Atmospheric Reactions of Fluorocarbons (completed).

Reaction rate constants have been measured for the reactions of $O(^1D)$ with CFCs 11, 12, 22, 113, and 114, and of OH with CFCs 11, 12, and 22. The results indicate that in the stratosphere the reaction of $O(^1D)$ atoms with CFCs 11 and 12 is secondary to photolysis, whereas the reaction of OH with CFC 22 is much more important than photolysis. The photooxidation products of 11, 12, and 22 at 184.9 nm, i.e., $COFCl$ and COF_2 as appropriate, are also observed to be the products for reaction with $O(^1D)$.

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 77-190. Atmospheric Chemistry of Peroxynitric Acid (completed).

The HO_2NO_2 cross sections vary smoothly from $1.6 \times 10^{-17} \text{ cm}^2 \text{ molec}^{-1}$ at 190 nm to $\sim 2 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1}$ at 330 nm. The infrared cross sections for the 802.7 and 1303.9 cm^{-1} Q branches of HO_2NO_2 at 0.06 cm^{-1} resolution are 2.1×10^{-19} and $1.8 \times 10^{-18} \text{ cm}^2 \text{ molec}^{-1}$, respectively.

Dr. A. R. RAVISHANKARA -- Georgia Institute of Technology -- 80-295. A Study of the Reaction of OH with ClO .

The rate constant for the overall reaction $OH + ClO \rightarrow \text{Products}$ and for the branch forming $HCl + O_2$ as products will be determined in a discharge flow system. Microwave interferometry, a novel technique, will be used in determining the concentration of HCl .

Dr. F. STUHL -- University of Bochum -- 77-170. Determination of the Photodissociation Process and Absorption Cross Section of FC-11 and 12 in the Near UV (completed).

The absorption spectra of some chlorine containing methanes (CCl_4 , $CHCl_3$, CH_2Cl_2 , CFC 13, and CFC 31) and ethanes (CFC 113, CFC 114, CFC 115, CFC 133a, and CFC 142b) and also of N_2O were determined at wavelengths around 220 nm. Some of these spectra were obtained at both 298 and 208°K. A chemical method was used to determine the absorption cross section of CFC 11 at 253.7 nm and the absorption properties at wavelengths greater than 280 nm. It is concluded from these experiments that the tropospheric decay rate of CFC 11 is smaller than 10^{-10} s^{-1} for homogeneous gas phase photolysis.

Table 3 (continued)

Dr. G. A. TAKACS -- Rochester Institute of Technology
-- 77-196. Photoabsorption Cross Sections for Compounds
of Atmospheric Interest (completed).

Ultraviolet-visible absorption spectra have been measured and solar photodissociation rates have been calculated for SO_2Cl_2 , CCl_3NO_2 , CF_3NOCl , SOCl_2 , SO_2F_2 , SO_2ClF , $\text{CH}_3\text{SO}_2\text{Cl}$, and CCl_3SCl . A maximum photoabsorption cross section, which indicates a long stratospheric lifetime, has been established for HClO_4 . Attempts to measure photoabsorption spectra for gaseous $\text{ONO}(\text{SO}_2)\text{OH}$ and $\text{ONO}(\text{SO}_2)\text{Cl}$ were unsuccessful. Photolysis of CFC 11 and CCl_4 in the presence of solid NaCl with wavelengths longer than 300 nm results in maximums of 2.3×10^{-4} and 2.4×10^{-4} molec, respectively, photodissociating per incident photon on the NaCl .

Dr. B. A. THRUSH -- University of Cambridge -- 75-58,
75-58II. Reactions of the HO_2 Radical Studied by Laser
Magnetic Resonance (completed).

The rate coefficient of the reaction $\text{O} + \text{HO}_2$ has been measured for the first time. The value found, $3.5 \pm 1.0 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 293°K, improves the fit of the calculated OH profile with Anderson's recent measurements. The rate coefficient of the reaction $\text{OH} + \text{HO}_2$ has been measured based on direct measurement of HO_2 and found to be $5.1 \pm 1.6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 293°K.

Dr. J. WIESENFELD -- Cornell University -- 76-128,
77-220. Photochemistry of Small Chlorinated Molecules
(completed).

The photochemistry of chlorine nitrate was studied by determining the yields of Cl and ClO from the flash photolysis of ClONO_2 . The rate of reaction between O and ClONO_2 has been measured and is in good agreement with the literature value.

Dr. R. ZELLNER -- University of Goettingen -- 77-195.
Experimental Investigation of the Branching Ratio in
the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ Reaction (completed).

The branching ratio in the reaction $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{HO} (1)$ and $\rightarrow \text{H}_2 + \text{O}_2 (1')$ has been determined at 298°K from direct measurements of HO and H_2 to be 0.01 ($k_1/k_{1'}$) (+0.005, -0.01). The main conclusions to be drawn from this result are:

1. Reaction 1' is not an important source of H_2 in the upper stratosphere and mesosphere.
2. The reduction of mesospheric HO_x through the occurrence of reaction 1' is not large enough to account for discrepancies in calculated and measured O_3 concentrations.

Table 3 (continued)

B. Source and Sink Studies

Dr. P. AUSLOOS -- National Bureau of Standards --
77-186, 78-254. Follow up for Photodecomposition
of Chloromethanes Absorbed on Silica Surfaces (com-
pleted).

The decomposition of CF_2Cl_2 , CFCl_3 , CH_3Cl , CCl_4 , CH_3CCl_3 ,
and CH_2CCl_2 on Tunisian sand at dilute concentrations (100
ppb - 100 ppm) has been investigated in both the presence
and the absence of light and/or moisture. Experiments with
 $^{13}\text{CCl}_4$, $^{13}\text{CFCl}_3$, and $^{13}\text{CF}_2\text{Cl}_2$ in the presence of oxygen show
that one molecule of $^{13}\text{CO}_2$ is produced per halomethane molecule
destroyed on the surface. For CH_3CCl_3 , surface destruction
leads to CH_2CCl_2 rather than CO_2 .

Under all conditions relative stabilities were as follows
 $\text{CF}_2\text{Cl}_2 > \text{CFCl}_3 > \text{CCl}_4 > \text{CH}_3\text{CCl}_3$. Both with and without light
the rate of surface-induced destruction decreases rapidly with
increasing moisture content. When the chlorofluoromethanes
were exposed to sand with a moisture content in equilibrium
with laboratory air (35% humidity at 20°C), no decomposition
was observed. However, a sudden reduction in moisture con-
tent by 40% or more leads to a measurable destruction rate
for CCl_4 and CH_3CCl_3 .

Dr. J. W. BIRKS -- University of Illinois -- 76-117B.
Studies of Heterogeneous Reactions (completed).

Potentially important heterogeneous reactions were studied.

The value of ϕ for the reaction $\text{ClONO}_2 \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \text{HOCl} + \text{HONO}_2$
lies in the range 2×10^{-4} to 10^{-3} .

Dr. M. J. CAMPBELL -- Washington State University --
75-53. Chlorofluoromethane Destruction by Natural
Ionization (completed).

Laboratory measurements at high irradiation levels show large
rate constants for removal of CCl_4 and CFC 11. The rate con-
stant for CFC 12 is much smaller. The significance of these
results with respect to atmosphere sinks for the CFCs is
questionable.

Drs. D. M. CUNNOLD, F. N. ALYEA, and R. G. PRINN --
CAP Associates -- 77-213, 78-251, 79-281, 80-323.
Coordination and Analysis of Data for the Atmospheric
Lifetime Experiment (ALE).

The tabulated data from the five automated long-term ground
measurement stations [cf. 79-280 (Lovelock and Simmonds,
p. 19) and 79-279 and 79-263 (Rasmussen, p. 21)] are being
completed, archived, checked statistically to aid in evaluat-
ing the performance of the network, and analyzed at least
annually for trends and approximate global concentrations.
Where possible, lifetime estimates will be calculated along
with their confidence ranges.

Table 3 (continued)

The 8-box tropospheric model (see Cunnold, et al., 78-252, p. 38) has been utilized to calculate that the average trend for CFC 11 from the five monitoring stations should be representative of the global trend with an accuracy of at least 0.5%/yr. The 8-box model will be used to prepare other estimates for the sensitivity of the ALE. Recommendations for calibration and data reporting in ALE have been made.

Measurement precision is good for the data processed up to June 1980. The measurement time sequence is not yet sufficient for accurate lifetime calculations. Preliminary indications are that CFC 11 may have a lifetime about half that expected from stratospheric photolysis alone, but with 2 σ error limits of 7 years to infinity. Seasonal variations that correlate well with air motions between the hemispheres are observed at all stations.

Dr. R. J. DONOVAN -- University of Edinburgh -- 79-286.
Reaction of ClO with OH: A Potential Sink for ClO_x.

A laboratory investigation, using flash photolysis, will be made of the ClO/OH reaction. Temperature and pressure dependence and the nature of the reaction products will be determined to elucidate further the mechanism of the reaction.

Dr. M. KAUFMAN -- Emory University -- 76-126, 77-197.
Studies of Compounds of Sulfur, Oxygen, and Chlorine (completed).

The three body recombination rate constant for Cl and SO₂ at 295°K has been found to be $1.3 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ with Ar, $2.3 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ with N₂, and $19 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ with SO₂. At 281°K the first and third values become 2.9×10^{-33} and 20×10^{-33} , respectively. Ultraviolet cross sections of SO₂Cl₂ and HOSO₂Cl have been determined, and the incorporation of ³⁶Cl into sulfate-type aerosol particles has been studied. Surface effects appear to have dominated the latter experiment.

When OCS is added to a Cl/Cl₂/Ar mixture at room temperature, SCl⁺ and SCl₂⁺ ions are detected mass spectrometrically. The rate constant for the reaction Cl + OCS → SCl + CO is less than $10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 296°K.

Dr. F. KORTE -- Technical University of Munich -- 77-194.
Photodegradation of Chlorofluoromethanes in the Troposphere (completed).

The photodegradation of CFC 11 and CFC 12 on silica gel and on Mecca sand was studied with the aid of ¹⁴C-labelled compounds. Whereas in the dark no change was determined with silica gel, there was significant decomposition on the sand with formation of ¹⁴CO₂ (up to 50%). Irradiation with UV

Table 3 (continued)

($\lambda > 290$ nm) led to 1-5% decomposition of the CFCs on silica gel also with formation of $^{14}\text{CO}_2$. Irradiation with UV was not observed to increase the decomposition rate on sand. The results suggest that decomposition takes place at active sites on the surface.

Dr. M. J. KURYLO -- National Bureau of Standards -- 78-233. Rates of Reaction of Cl Atoms with the Primary Products of Alkane Photooxidation (completed).

See Table 3, Section A (p. 14).

Dr. J. E. LOVELOCK -- University of Reading -- 75-67, 77-144. Unidentified Factors in the Fluorocarbon-Ozone Problem (completed).

Coarse Saharan surface dust showed an unusual degree of retention for CFC 11 and CCl_4 . Investigations were made on the relationship between photochemically produced atmospheric peroxy compounds (e.g., peroxyacetyl nitrate) and the incidence of skin carcinoma.

Observations on dissolved gases in the ocean were made during the April 1977 voyage of RRS Challenger. Concentrations of N_2O in ocean and atmosphere confirmed earlier estimates of N_2O flux from the ocean.

Dr. J. E. LOVELOCK and P. G. SIMMONDS -- Private -- 77-193, 78-243, 79-280, 80-324. Operation of Stations in Adrigole and Barbados for the Atmospheric Lifetime Experiment.

Automated long-term ground measurement stations are being operated in Adrigole (continuing the data base already collected there) and in Barbados. Hewlett-Packard electron-capture gas chromatographs are being used to collect data for CFCs 11, 12, and 113, CH_3CCl_3 , CCl_4 , and N_2O , which are processed, tabulated, and forwarded to CAP Associates for analysis.

Both stations are operating well with data being processed from March 3, 1978 (Adrigole) and July 12, 1978 (Barbados). Battery back-up protection has been installed at both stations to minimize problems from power interruptions. Several details that are important to the continuous operation of remote stations have been identified, and maintenance procedures are being modified appropriately. Adrigole data are affected more by air pollution events than the other remote stations, and techniques to handle such events are being developed. Barbados data show the expected small variability.

Table 3 (continued)

Dr. L. R. MARTIN - Aerospace Corp. -- 75-81, 75-81II.
Laboratory Investigation of the Heterogeneous Interaction of Cl and ClO with H₂SO₄ (completed).

A flowing afterglow apparatus was used to measure the rate of the heterogeneous reactions of Cl and ClO with sulfuric acid, simulating the stratospheric aerosol. The reaction rate of Cl is too slow for its reaction to constitute a significant sink, although rates were markedly increased by the presence of certain metal salts in the sulfuric acid. Even at stratospheric temperatures the HCl formed goes into the vapor phase. The ϕ for ClO on H₂SO₄/H₂O substrates is 1×10^{-3} at room temperature. These, the first examples of heterogeneous reactions with stratospheric aerosol, are not in any models.

Dr. V. A. MOHNEN -- State University of New York, Albany -- 75-64. Ion Molecule Reactions Involving Fluorocarbons (completed).

Ion molecule reactions between the equilibrium ion distribution formed in pure air-like gas mixtures and CFC 12 were studied. From these investigations it was concluded that: (1) stable CFC 12 attachments to ions ("cluster formation") of the form $H^+ \cdot (H_2O)_n$, $O_2^- \cdot (H_2O)_n$, $CO_3^- \cdot (H_2O)_n$, and $CO_4^- \cdot (H_2O)_n$ do not occur; (2) dissociative charge transfer reactions between $H^+ \cdot (H_2O)_n$ and CFC 12 are not observed for all $n > 2$; (3) approximate rate constants for dissociative charge transfer reactions between CFC 12 and $O_2^- \cdot H_2O$ and CFC 12 and CO_3^- are $3 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ and $< 2 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$, respectively; (4) knowledge of time integrated rate constants for atmospheric negative ions is necessary before the importance of ion reactions with CFCs can be estimated, but the likelihood of substantial importance is small.

Dr. L. F. PHILLIPS -- University of Canterbury (NZ) -- 78-241. Determination of Atomic Oxygen Yields in the Photolysis of HOCl and ClOO (completed).

The photolysis was studied by looking for prompt O atoms by observation of resonance fluorescence on a nanosecond time scale. Detection limits for ground-state oxygen atoms produced by photolysis of NO₂ were established.

Gaseous mixtures containing HOCl were photolyzed with UV radiation at 337 nm from a nitrogen laser to determine whether the HOCl \rightarrow HCl + O reaction path occurred. Because the signal to noise ratio was too low, attempts to measure oxygen atoms by resonance fluorescence gave inconclusive results. Recommendations were made for improving the sensitivity of the detection method in future studies.

Table 3 (continued)

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 75-12. Monitoring and Atmospheric Reactions of Fluorocarbons (completed).

CFCs 11 and 12 are photochemically stable in simulated sunlight, even when irradiated for several weeks. Plant tissues did not absorb measurable quantities of CFCs 11, 12, or 22, and no adverse effects could be measured. CFCs penetrate into the soil atmosphere, and concentrations change in direct relationship with changes in concentration in the atmosphere above ground.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-71. Measurement of Fluorocarbon Content of "Antique" Air Samples (completed).

A sensitive method for the determination of low parts per trillion analysis of CFCs 11 and 12 in small-volume air samples in containers was developed and applied to a wide variety of vessels believed to contain antique air. All samples analyzed showed varying levels of CFCs. Contamination during handling is not a problem, so that either CFCs were present in nature prior to 1930 or the samples were contaminated by leakage during storage.

Dr. R. A. RASMUSSEN -- Rasmussen Associates -- 75-84. Collection and Analysis of Antarctic Ice Cores (completed).

The concentration of halocarbons in air obtained from Antarctic snow shows no enrichment in samples obtained from the Ross ice shelf (mainly -30°F), whereas there is enrichment in samples obtained from the South Pole (-50 to -60°F).

Dr. R. A. RASMUSSEN -- Private -- 76-140. Lower Stratospheric Measurement of Non-methane Hydrocarbons (completed).

Ethane, ethylene, and acetylene are found in the upper troposphere and lower stratosphere at concentrations of 40-820 ppt. Total concentrations of the three species range from 1085 ppt (NH troposphere) to 323 ppt (SH stratosphere).

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 77-201, 78-248, 78-263, 79-279, 80-325. Operation of Stations in American Samoa, Cape Meares, Oregon, and Tasmania for the Atmospheric Lifetime Experiment.

Automated long-term ground measurement stations are being operated in American Samoa and Tasmania as detailed in 77-193 (Lovelock and Simmonds, p. 19). Data have been processed from May, 1978, (Tasmania) and June, 1978, (American Samoa) up to June, 1980.

Table 3 (continued)

The fifth ALE station at Cape Meares, Oregon, became operational early in 1980 and is now contributing measurement data routinely to the ALE network.

Dr. R. A. RASMUSSEN -- Oregon Graduate Center --
77-215. Kilauea Volcanic Emissions -- Halocarbon
Measurements (completed).

Electron capture gas chromatograph analyses were made on fumerolic emissions from two vents on Kilauea at the site of the September, 1977 lava flow. Some 20 halocarbons were observed and compared with local control samples. CFCs 11 and 12, CCl_4 , and CH_3CCl_3 were not significantly different from controls. Peaks tentatively identified as N_2O and methyl halides showed elevated concentrations versus controls. The presence of N_2O was confirmed by GC-MS.

Dr. C. SANDORFY -- University of Montreal -- 73-2.
Spectroscopy and Photochemical Changes of Fluoro-
carbons (completed).

The vacuum ultraviolet and photoelectron spectra of CFCs were measured. The photochemical vulnerability of these molecules was predicted from their spectra.

R. E. SHAMEL -- A. D. Little, Inc. -- 79-275. Analysis
of Release of FC-11 from Rigid Plastic Foam Products in
the U. S. (completed).

The lifetime for CFC-11 emissions from rigid foam is much longer than previously assumed and will not be a problem for the ALE lifetime calculations.

Drs. P. G. SIMMONDS and J. E. LOVELOCK -- Private --
79-269. Determination of Tropospheric Halocarbons
and Their Relative Importance.

See Table 3, Section C (p. 27).

C. Laboratory Studies Related to Potential Atmospheric Measurements

Dr. J. W. BIRKS; Drs. C. J. HOWARD and F. C. FEHSENFELD
-- University of Colorado; National Oceanic and Atmos-
pheric Administration, Boulder -- 77-222. Development
of a Technique for Measuring the Total Chlorine Content
in Air.

The goal of this project is to develop an analytical instru-
ment for measuring the total chlorine content of whole air.
In principle a gas stream will be passed through a discharge
plasma, and chlorine emission lines in the vacuum UV region

Table 3 (continued)

will be used to determine chlorine content. The equipment consists of a UV monochromator, discharge source, and resonance fluorescence detector.

The chlorine signal response has been investigated for a number of different chlorine-containing compounds, and the linearity of the total chlorine signal is under investigation.

Dr. H. L. BUIJS -- Bomem, Inc. -- 75-90. Construction of a Fourier Transform Spectrometer (completed).

A spectrometer with a projected resolution of 0.02 cm^{-1} was constructed for use in the simultaneous determination of ClONO_2 and either HCl or HF , or of HCl and HF . See Table 3, Section D (p. 31).

Dr. H. L. BUIJS -- Bomem, Inc. -- 77-168. Measurement of Halogen Compounds for Determination of Total Chlorine and Total Fluorine in the Stratosphere Using Long-Path Interferometric Spectroscopy (completed).

A library study has shown that there are very few published experimental data of sufficient resolution and quality for the interpretation of solar IR spectra.

Dr. H. L. BUIJS -- Bomem, Inc. -- 77-221. Measurement of Infrared Spectra of Selected Stable Molecules.

Fourier transform infrared spectra of methyl chloride in the $3.3 \text{ }\mu\text{m}$ region and of phosgene, carbonyl chlorofluoride, and carbonyl fluoride in the $1.3 \text{ }\mu\text{m}$ to $5.6 \text{ }\mu\text{m}$ region have been recorded at 0.01 cm^{-1} resolution both at room temperature and at stratospheric temperature ($\sim 240^\circ\text{K}$). The low-resolution spectrum of methyl chloroform from about $2.1 \text{ }\mu\text{m}$ to $5.6 \text{ }\mu\text{m}$ showed no useful features for detection of this species in the atmosphere.

Dr. J. A. COXON -- Dalhousie University -- 78-255, 80-315. The $\text{A}^2\Pi_i \rightarrow \text{X}^2\Pi_i$ Band System of ClO : Absolute Absorption Cross Sections at High Resolution for Bands of Stratospheric Interest.

Equipment and facilities for spectroscopic work on the ClO radical have been assembled. ClO has been generated in a fast flow system from the reaction $\text{Cl} + \text{OClO} \rightarrow 2\text{ClO}$. Both ^{35}ClO and ^{37}ClO will be investigated, particularly at $\lambda > 290 \text{ nm}$. Preliminary absorption traces of the $\text{A}^2\Pi_i \rightarrow \text{X}^2\Pi_i$ band system of ClO have now been recorded at high resolution. Several bands, 11-0 to 4-0 in the $^2\Pi_{3/2}$ subsystem, have been identified. The absorption intensity of these bands is high. Even from this preliminary work it is possible to establish an important new

Table 3 (continued)

result: the width of individual lines in a vibrational band appears to be greater than previous estimates made from photographic plates. Systematic measurements of ClO absorption intensities (especially for the bands of stratospheric interest) and the calculation of absolute absorption cross sections are in progress. These data would assist continuous monitoring of ClO from high altitude platforms.

Dr. D. D. DAVIS -- University of Maryland -- 74-10. Laboratory Determination of the Sensitivity of Laser-Induced Fluorescence for the Detection of ClO under Atmospheric Conditions (completed).

Ground-state stationary ClO concentrations of about 10^{12} cm^{-3} were scanned at several electronic absorption wavelength regions with a tunable UV laser. Laser-induced fluorescence proved to be unusable for measuring ClO.

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-73. Laboratory Measurement of Spectroscopic Absorption Cross Sections of ClO (completed).

A frequency doubled tunable dye laser with a band width of 0.0015 nm was used to measure the absorption cross sections of ClO as a function of wave length for the $A^2\Pi_{3/2} \ 9-0$ band. There was overall lack of resolution in the data, and an unassigned peak was observed at 283.06 nm. Simulated spectra indicated that a baseline resolved spectrum is not feasible, that the unassigned peak could be a ^{37}ClO absorption, and that the ^{35}ClO line width is somewhat wider than reported by Coxon and Ramsay. The real cross section attributable to ^{35}ClO at 282.94 nm (the largest peak in the spectrum) is calculated to be $\sigma_{19.5}^R = 1.04 \times 10^{-16} \text{ cm}^2$.

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-87. Development of Instrument for Stratospheric OH Measurement by Laser-Induced Fluorescence (completed).

A miniaturized dye laser module for balloon flights has been built and tested.

Dr. A. E. J. EGGLETON -- Atomic Energy Research Establishment, Harwell -- 76-116. Total Chlorine Measurements in the Troposphere and Stratosphere (completed).

The feasibility of measuring total chlorine and fluorine in the atmosphere by neutron activation and γ photon activation, respectively, after collection of reactive species and particulate material on filters and collection of gaseous compounds on activated charcoal was studied. The proposed

Table 3 (continued)

method proved unsuitable for the determination of total chlorine and fluorine contained in unreactive organic compounds due to a combination of insufficiently low halogen blank values in the best activated charcoal prepared and to inadequate adsorptive capacity for the more volatile organic compounds.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 75-47. Laboratory Determination of the Feasibility of Laser Magnetic Resonance for ClO Detection and Reaction Studies (completed).

It has been demonstrated that ClO can be detected by laser magnetic resonance with a sensitivity of about 10^{10} molec cm^{-3} . Current maximum model predictions are about 10^8 molec cm^{-3} , and measurements have approached 10^9 molec cm^{-3} at 30 km.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 80-299. Infrared Spectroscopy of Atmospheric Species.

This measurement program is to provide accurately calibrated high-resolution infrared spectra of shorter lived atmospheric species for the identification and quantification of these constituents in the stratosphere. A Fourier transform infrared spectrometer is to be obtained. The first species to be studied is peroxyxynitric acid. (This project is dependent on the acquisition of appropriate cofunding.)

Dr. H. D. KNAUTH -- University of Kiel -- 77-171. Laboratory Study of the UV and IR Spectra of HOCl, HOONO₂, and HClO₄ in the Temperature Range of the Stratosphere (completed).

It was not possible to obtain partial pressures of HO₂NO₂ greater than 0.1 torr in the N₂O₅/H₂O₂ system in Pyrex vessels. The spectrum for gaseous HOCl was derived from extinction measurements on the Cl₂/H₂O system at 333°C for different values of the equilibrium constant for the reaction $\text{H}_2\text{O} + \text{Cl}_2\text{O} \rightarrow 2\text{HOCl}$. The results are not in complete agreement with those of Timmons (76-129, p. 28), so additional work on the absorption centered around 300 nm is required.

Dr. H. D. KNAUTH -- University of Kiel -- 77-224. Laboratory Study for Determination of the Equilibrium Constant of the Reaction $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HOCl}$ and the UV Spectrum of HOCl (completed).

The gas phase system $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2\text{HOCl}$ has been investigated by UV from 200 to 500 nm at 333°K. Isobestic points were found at 214, 233, 335, and 380 nm. The equilibrium

Table 3 (continued)

constant 0.132 ± 0.008 and HOCl cross sections were derived from absorbance measurements of the mixtures at equilibrium. The resulting HOCl spectrum shows absorption bands with peaks at 240 and 310 nm. Very clean $\text{Cl}_2\text{O}/\text{H}_2\text{O}/\text{HOCl}$ mixtures proved to be remarkably stable. Thermal decomposition produced Cl_2 with intermediate formation of ClO_2 . The absorption cross sections of Cl_2O , ClO_2 , and Cl_2 were determined separately at 333°K.

Dr. J. E. LOVELOCK -- Private -- 76-120. The Electron Capture Detector as a Reference Standard for Analysis of Atmospheric Halocarbons (completed).

A theoretical model of the operation of the electron capture detector was developed. Application to the procedure used at the Adrigole station and on the RV Shackleton (1971-2) indicate that measurements at these bases are within 3% of theoretical predictions for CCl_4 and CFC 11. This evaluation was extended to CH_3CCl_3 measurements.

Dr. J. E. LOVELOCK -- Private -- 78-226, 78-264, 80-293. Development of Primary Fluorocarbon Standards.

An exponential dilution technique, using a converted barn as the dilution chamber, has been developed to provide primary standards for halocarbon concentration measurements.

During what had been expected to be the final phase of measurements on CFC-11 and CFC-12, measurements outside the previously accepted error limits were obtained. A review of the experimental procedures to identify hitherto undetected sources of systematic error has been made. None was found with the possible exception of water contamination of fluorocarbon samples during transfer. Final measurements are now expected to be completed before the end of the year.

Dr. K. MOE -- Private -- 78-235. Effect of Aerosol Scattering on Ozone Measurements with the Dobson Spectrophotometer (completed).

The NCAR UV double monochromator (UVDm) and associated computer programs have been shown to be capable of ozone measurements of hitherto unobtainable accuracy, while simultaneously measuring aerosol optical depth as a function of wavelength in the region of strong ozone absorption. An ozone value of 0.328 ± 0.006 cm was obtained at 10:00 h MST for June 8, 1978 compared with a corrected Dobson measurement of 0.340 cm at 12:05 h MST.

The increasing number of UVDm's being deployed could provide accurate ozone data to resolve the discrepancy between predictions of ozone decrease from photochemical models and Dobson measurements, which show no decrease or increase.

Table 3 (continued)

Dr. D. G. MURCRAY -- University of Denver -- 75-92, 77-152, 78-265. Laboratory Measurement of High Resolution Infrared Spectra of Chlorine-Containing Molecules of Stratospheric Interest.

Laboratory measurements of the high resolution infrared spectra of chlorine-containing molecules are being made. Statistical-band-model analyses and integrated intensity measurements for the 10.8 μm band of CFC 12 and 11.8 μm band of CFC 11 have been published. The spectrum of H_2O_2 has been measured. A compendium of laboratory IR spectra (resolution 0.04-0.06 cm^{-1}) has been prepared. A list of compounds measured as well as detailed spectra are available to investigators upon request to CMA, attention J. C. Van Horn.

Dr. R. W. NICHOLLS -- York University -- 75-11 and 75-11-II. Experimental and Theoretical Studies on the UV Spectrum of ClO with Stratospheric Applications.

Absolute absorption coefficients and cross sections have been measured for all bands and the photodissociation continuum of the $\text{V}''=0$ progression for ClO . The very complicated emission spectrum that has been excited over the wavelength range 2500-4500 \AA in discharges through ClO_2 and Cl_2O is currently undergoing measurement, identification, and analysis. Computer-based synthetic spectra of various ClO bands have been calculated. Current work, which emphasizes the (2,0), (3,0), and (4,0) bands, should be of immediate diagnostic application to ground-based and balloon-based stratospheric spectroscopic observations.

Dr. R. W. NICHOLLS -- York University -- 75-30b. Laboratory Studies of the Infrared Vibration-Rotation Spectrum of ClO (completed).

Work in this area was suspended to allow greater effort in the UV measurements (75-11).

Dr. R. A. RASMUSSEN -- Private -- 76-142, 78-247. Interlaboratory Comparison of Fluorocarbon Measurements (completed).

A second round of identical samples of rural air has been circulated blind to participating laboratories for analysis for CFCs 11 and 12, CHCl_3 , CH_3CCl_3 , CCl_4 , and N_2O . Overall the results obtained showed a spread similar to that obtained in the 1976 NASA workshop. However, as in 1976, there was excellent agreement between Rasmussen and Lovelock, who use two different methods of calibration. A third round of

Table 3 (continued)

samples was analyzed by 19 laboratories. Good agreement ($\pm 5\%$) was obtained by the 5 laboratories using common primary standards, but the other 14 laboratories showed much larger variations, with mean values considerably lower than those of the 5 laboratories.

Drs. P. G. SIMMONDS and J. E. LOVELOCK -- Private --
79-269. Determination of Tropospheric Halocarbons
and Their Relative Importance.

New methods are to be sought for the improved measurement of halocarbons that are not presently determined with sufficient sensitivity by EC/GC. Techniques will evaluate enhancement of EC sensitivity by cryotrapping, selective adsorbents, the use of "doped" carrier gas, and chemical conversion. The first priority is to improve routine monitoring of CH_3Cl .

New techniques such as the electrolytic conductivity detector (which could also provide the basis of a total chlorine monitor) and the photoionization detector will also be evaluated. It is hoped that these new techniques will permit future routine monitoring of a wider range of both natural and anthropogenic halocarbons.

Laboratory development experiments on the doping and cryogenic/adsorbent techniques for methyl chloride continue to make good progress. Attempts to increase detection sensitivity by chemical conversion of methyl chloride to methyl iodide have so far proved unsuccessful. A preliminary evaluation of the photoionization detector, using a borrowed instrument, showed this method of detection to be unpromising, and a new instrument will therefore not be purchased.

Dr. R. K. SKOGERBOE -- Colorado State University --
77-206. Development of a Measurement System for the
Determination of Total Chlorine in Air (completed).

The technique involves two flame reactions. The first, in a H_2 -rich flame, forms HCl , which is treated with indium to yield InCl . The InCl is then excited in an air-rich flame and detected photometrically. Blind analyses of calibration samples proved that the sensitivity of the technique was not sufficient to be of value for stratospheric measurements. However, it is hoped that the system can be put to use in tropospheric monitoring.

Dr. D. H. STEDMAN -- University of Michigan -- 74-7.
Atmospheric Determination of ClO Concentration: A
Feasibility Study (completed).

Laboratory studies have demonstrated the feasibility for detecting stratospheric ClO by chemical conversion to Cl (by reaction with NO) accompanied by vacuum ultraviolet resonance fluorescence. In-flight use of this technique is being supported by NASA.

Table 3 (continued)

Dr. D. H. STEDMAN -- University of Michigan - 76-132.
Absolute Calibration of Fluorocarbon Measurements
(completed).

A feed-back flow system for the calibration of CFC samples
has been built.

Dr. D. H. STEDMAN -- University of Michigan -- 77-151.
Generation and Exchange of Calibrated Samples of
Fluorocarbons (completed).

Work on this project was stopped because of feasibility
problems.

Dr. R. B. TIMMONS -- Catholic University -- 76-129.
Photochemical and Chemical Kinetics Measurements of
Stratospheric Importance with Respect to the Fluoro-
carbon Issue (completed).

HOCl is a possible stratospheric sink the magnitude of which
would depend on the absorption cross section. Earlier
spectral measurements were inaccurate. Pure HOCl cannot be
prepared, for an equilibrium mixture of Cl₂O and HOCl exists.
The equilibrium constant for this reaction is $K_p \approx 0.8$.
This value and the UV absorption cross sections of Cl₂O have
been used to determine the UV absorption cross sections of
HOCl between 200-330 nm. The 230-240 nm peak was lower than
previously measured, and no peak was found at 320 nm.

Dr. R. B. TIMMONS -- University of Texas, Arlington --
77-214, 78-258. Photochemical and Chemical Kinetics
Measurements of Stratospheric Importance with Respect
to the Fluorocarbon Issue.

The UV absorption cross sections of HOCl between 200-330 nm
over longer pathlengths are being determined under condi-
tions such that interference by Cl₂O is minimal, i.e., low
Cl₂O concentration and excess H₂O. An induction period for
the increase in UV absorption at 320 nm is observed, sug-
gesting that the 320 nm absorption may be due to more than
one species.

The equilibrium constant for the Cl₂O + H₂O reaction appears
to be essentially temperature independent over the tempera-
ture range 25 to 57°C.

Work is in progress using a quadrupole mass spectrometer
toward the direct determination of the concentration of
HOCl and any other interfering species, thus making the
measurement of the UV absorption cross section more accurate.

Table 3 (continued)

Dr. R. J. SAYKALLY -- University of California, Berkeley -- 80-300. Near- and Far-Infrared Spectroscopy.

This project seeks to develop far-infrared laser electric resonance as a technique for detection and measurement of transient species, with parallel work in tunable F-center laser spectroscopy. Species chosen for the studies are HOCl, HO₂, OH, and CH₃O. The methods have potential applications in both laboratory kinetics and stratospheric measurements.

Drs. W. A. TRAUB and K. V. CHANCE -- Smithsonian Astrophysical Observatory at Harvard University -- 80-318. Far-Infrared Laboratory Spectroscopy of Halogen-Containing Molecules.

Laboratory spectra of HCl, HOCl, and ClONO₂ will be studied at a resolution of about 0.03 cm⁻¹ in the region 70 to 250 cm⁻¹, in order to establish the positions, strengths, and pressure broadening effects of air on the lines and bands. This work is done in support of an ongoing balloon measurement program.

D. Tropospheric and Stratospheric Measurements

Dr. J. E. BECKMAN -- Queen Mary College, London -- 79-282. Airborne Millimeter-Wave Determination of ClO.

Airborne observations of ClO using a 241 GHz receiver will be made. This equipment will be flown "piggyback" on a NASA aircraft (C141) flight scheduled for late October 1980.

Drs. A. BONETTI and B. CARLI; Dr. J. E. HARRIES -- University of Florence, Consiglio Nazionale delle Ricerche, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy; National Physical Laboratory, U. K. -- 76-137, 80-297. Submillimeter-Infrared Balloon Experiment.

Vertical distributions and diurnal variability of H₂O, O₃, NO₂, HNO₃, HCl, CFCs 11 and 12, ClO, ClONO₂, and other molecules are being determined using the 9 to 15 micron infrared region and submillimeter wavelengths from 200 to 1000 microns. Data from the October 1978 flight have been reduced for CFCs 11 and 12, O₃, and HNO₃.

Laboratory measurements of the rotational spectra of molecular species relevant to stratospheric chemistry and photochemistry will be carried out in the spectral interval 5 to 80 cm⁻¹ with possible extension to 120 cm⁻¹ with a resolution of 0.0033 cm⁻¹ up to 40 cm⁻¹ and with a resolving power of 1,210⁴ beyond 40 cm⁻¹. The spectra will be produced through the same Submillimeter Polarising Interferometer employed in the stratospheric flights.

Table 3 (continued)

Dr. F. BRUNER -- Urbino University -- 78-256. Determination of F-21 and Other Halocarbons in the Troposphere (completed).

Two analytical methods for the quantitative determination of atmospheric CFC-21 at 1-50 ppt concentration have been set up based on GC separation followed, respectively, by EC and MS. In both methods the permeation tube technique has been adopted as the primary quantitative standard.

A series of samples have been collected from rural and industrial areas in Italy and over the Red Sea and the Indian Ocean. Concentrations of CFC-21 ranged from a few ppt to as great as 40-50 ppt.

Dr. H. L. BUIJS - Bomem, Inc. -- 75-90, 75-98. Measurement of HCl and HF in the Stratosphere by Fourier Transform Spectroscopy (completed).

Balloon flights to Alaska (May 1976) and New Mexico (September 1976 and March 1977) have provided profiles for HF and HCl concentrations. The HCl profile (volume mixing ratio), but not the HF profile, appears to show a maximum at 23-25 km, where the volume mixing ratios are 8×10^{-10} (HCl) and 10^{-10} (HF). The HCl value is similar to values obtained by other investigators.

Upper limits on the concentrations of C_2H_6 and CH_3Cl are $\leq 0.6 \times 10^{-9}$ and $\leq 1 \times 10^{-9}$ (mole fraction), respectively.

See Table 3, Section C (p. 23).

Dr. H. L. BUIJS -- Bomem, Inc. -- 77-156. Operational Costing for Flights Planned in 1977.

HCl and HF profiles were recorded by infrared techniques from a balloon launched in New Mexico on October 27, 1978. The HCl mixing ratio increased from about 2×10^{-10} at 20 km to about 1×10^{-9} at 35 km. Similar values for HF are about 3×10^{-11} and 3×10^{-10} , respectively. The shape of the curve of HF/HCl vs. altitude is in reasonable agreement with that of Farmer and Raper (1977) over the altitude interval 17-27 km but does not agree with the profile calculated from models by Sze (1978).

Additional balloon flights are planned for simultaneous measurement of HCl, HF, and/or $ClONO_2$.

Table 3 (continued)

Dr. D. H. EHHALT -- Nuclear Research Establishment
Juelich -- 76-145. Electron Spin Resonance Detection
of Stratospheric Radicals (completed).

Under a program supported by the German Government's Department of Research and Technology a cryogenic sample was collected at 30.5 km at 1600-1700 hr (conditions of relatively low radical concentration) during Murcray's March 1977 balloon flight. The frozen sample was analyzed by ESR, showing the following concentrations. NO_2 : 3.5×10^8 ; HO_2 : 8.5×10^6 molec cm^{-3} ; ClO : not detected.

Dr. P. A. EKSTROM -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 75-27. Ground-Based Millimeter-Wavelength Observations of Stratospheric ClO (completed).

About 500,000 data points were obtained in the microwave spectra near 93 GHz with the Kitt Peak radiotelescope. Excessive noise made interpretation difficult, but base-line corrected spectra suggested an upper limit on ClO of one hundred times model predictions.

Dr. A. GIRARD -- Office National d'Etudes et de Recherches Aeronautiques, France -- 75-88. Measurement of HCl , HF , ClO , etc., in the Stratosphere by High Resolution Infrared Spectroscopy (completed).

Vertical profiles of HCl , NO_2 , H_2O , and CH_4 between 26 and 35 km have been deduced from two balloon-borne grating spectrometer experiments. There is a hint of a decrease in HCl mixing ratio at the upper limit of the October 1977 experiment. Laboratory infrared spectra have been obtained for ClNO_3 , NO_2 , HNO_3 , and HCHO . The method of infrared limb sun pointing was found to be inadequate for the detection of ClO in the atmosphere.

Drs. A. GOLDMAN and A. BARBE -- University of Denver; University of Reims, France -- 80-322. Collaborative Studies on Atmospheric Spectroscopy.

Atmospheric species such as O_3 , HCl , HF , NO_2 , NO , N_2O , HNO_3 , OCS , etc., are to be identified and quantified by their infrared absorption spectra. The work will cover a wide range of laboratory, ground-based, and theoretical studies and utilize the complementary skills and established collaboration between Denver and Reims.

Table 3 (continued)

Dr. P. JOUVE -- University of Reims, France -- 79-290.
Measurement of the Vertical Distribution of HCl, O₃, and
HCHO and the Ratio HF/HCl.

Ground-based measurements of HCl, HF, and other important species will be made using high resolution infrared spectroscopy. These measurements will be made during 1981 from an observatory in Haute Province, France, by a team from Jouve's group at the CNRS Laboratory located in Reims.

Dr. J. E. LOVELOCK -- University of Reading, Private
-- 73-1, 74-3, 75-67, 77-144. Fluorocarbons in the
Environment (completed).

The electron capture gas chromatograph (ECGC) has been developed and applied to the measurement of several halocarbons in the lower stratosphere and troposphere, particularly over Europe and the Atlantic Ocean. In 1976 levels of CFC 11 were about 130 ppt (U. K.) and 80 ppt (Southern Hemisphere). CH₃Cl, with the ocean and smouldering vegetation as identified sources, was at about 10⁻⁹ v/v in the Northern Hemisphere but was found to be higher over the southern African continent (2.2 x 10⁻⁹ v/v in Kenya) (cf. Rasmussen, 77-181, p. 35). CCl₄ and CH₃CCl₃ were also unexpectedly high. Portable monitoring equipment has been provided and put to use in South Africa and Australia. The levels of CH₃CCl₃ found in the Southern Hemisphere (50 ppt) appeared higher than expected from release and tropospheric lifetime estimates. Northern Hemisphere values were about 100 ppt.

Measurements of CFC 11 in the atmosphere and ocean were made during the April 1977 voyage of RRS Challenger in the northeast Atlantic Ocean. Average air concentrations of 155 ppt were observed for CFC 11, and it was present at saturation quantities down to depths of 500 m.

See Rasmussen 76-142, p. 27.

Dr. D. G. MURCRAY -- University of Denver -- 75-13,
76-101, 76-135, 77-166. The Measurement of the
Stratospheric Distribution of Fluorocarbons and
Other Constituents of Interest in the Possible
Effect of Chlorine Pollutants on the Ozone Layer.

Measurement of stratospheric distribution by balloon-borne, high-resolution, infrared absorption measurement at large solar zenith angles has been achieved using a specially constructed grating spectrometer. The distributions for CFCs 11 and 12 and CCl₄ obtained showed a concentration increase of about 2.5, with a rather wide range of uncertainty, from 1968 to 1975 for CFCs 11 and 12. Subsequent flights also yielded HCl and HNO₃ profiles. A preliminary value of ~2 ppbv for the concentration of ClONO₂ at 26 km has been calculated. The upper limit for H₂O₂ is 1 ppbv at 20 km.

Table 3 (continued)

An October 1978 balloon flight with an interferometer system instead of a grating system was successful and recorded through sunset with the last record obtained at solar zenith angle $>95^\circ$. A strong absorption at 1283 cm^{-1} is due to CF_4 with an estimated mixing ratio of 75 pptv at 25 km. The ClONO_2 mixing ratio is 0.8 pptv from 24 km to 32 km, then falling to 0.4 ppbv at 33.5 km. Several features coincide with some of the HOCl lines, but the agreement appears fortuitous, and no features can be assigned with certainty to HOCl . The upper limit for H_2O_2 is 0.5 ppbv at 20 km and for COF_2 is 0.4 ppbv at 25 km.

Dr. D. G. MURCRAY -- University of Denver -- 77-211.
Acquisition of an On-Board Digital Recording System
(completed).

The balloon-borne interferometer system has been improved by incorporating into it on-board recording capability. Advantages are two-fold: a back-up is provided in case the telemetry system malfunctions, and it becomes possible to operate under atmospheric wind conditions that might carry the balloon out of telemetry range. The system was used for a balloon flight October 28, 1978. Analysis of the recorded data indicates the unit meets design objectives.

Dr. D. G. MURCRAY -- University of Denver -- 78-228.
Detection of Selected Molecules by Ground-Based
Solar Spectroscopy (completed).

Solar spectra were examined with a resolution of 0.01 cm^{-1} . An atlas of the $775\text{--}950\text{ cm}^{-1}$ and $1050\text{--}1300\text{ cm}^{-1}$ regions has been prepared.

A workshop on solar spectroscopy was held at the National Bureau of Standards, March 26, 1980.

Drs. D. G. MURCRAY and H. K. ROSCOE -- University of Denver; Oxford University, England -- 77-219. Stratospheric HCl Measurements Conducted as a Piggy-Back to Murcay's Flight.

Because the vibration problem with the solar-absorption pressure modulator radiometer used for the HCl measurements could not be reasonably solved, this project was cancelled.

Drs. D. G. MURCRAY and H. K. ROSCOE -- University of Denver; Oxford University, England -- 80-328. An Inter-comparison of Measurements of Stratospheric HCl .

A simultaneous measurement of the HCl profile in the stratosphere will be made on a balloon flight. Murcay will utilize a high resolution IR interferometer, and Roscoe will use a pressure modulated radiometer.

Table 3 (continued)

Dr. R. A. RASMUSSEN -- Washington State University --
75-2, 75-59. Fluorocarbon Research (completed).

An attempt was made to obtain halocarbon concentration measurements as far into the stratosphere as could be reached by an available commercial aircraft. A small portable gas chromatograph was used for on-board measurements, and canister samples were collected for subsequent detailed halocarbon analysis on the ground. One phase of the study consisted of samples collected over a wide area of the Pacific Northwest, a second of samples collected frequently to the maximum attainable altitude over Alaska. The halocarbon concentrations are either constant or decrease very slowly with altitude in the tropopause, decrease rapidly in the tropopause from the tropospheric concentration to an average value identifiable with the stratosphere, and do not show a clear pattern of concentration gradients above the tropopause.

A trans-Pacific flight from 80°N to 60°S has been completed, and the air samples collected have been analyzed for halocarbons. Most of the samples were collected at 39,000 to 43,000 ft. CFC 12 concentrations are about 10% higher in the north than in the south at ground level, and the difference is apparently greater for CFC 11.

Dr. R. A. RASMUSSEN -- Private -- 77-181. Measurement of the Concentration of Methyl Chloride in Air in Kenya (completed).

Air samples were obtained at ground level and by aircraft in Kenya and over the Indian Ocean. Analyses showed CH₃Cl at 600-700 ppt over Kenya, rising to 900-2000 ppm in areas where slash burning was being conducted (cf. Lovelock, 77-144, p. 33). Boundary layer analyses over the Indian Ocean were 750-880 ppm. N₂O levels were 324-378 ppb. Other analyses showed CFC 12, 235-246 ppt; CFC 11, 137-143 ppt; CH₃CCl₃, 74-96 ppt; and CCl₄, 120-135 ppt. Comparison with previous data showed interhemispheric differences for the above five species.

Dr. R. A. RASMUSSEN -- Oregon Graduate Center --
78-260. Identification of FC-21 in the Atmosphere (completed).

Measurements of CFC 21 in Tasmania, at the South Pole, and in "clean" air from Cape Meares, OR, show concentrations of 0.05-0.6 ppt, compared with concentrations of 2 ppt at Harwell, U. K. GC/MS identification confirms CFC 21, distinguishing CFC 21 from CH₃I. CFC 21 samples do not increase in CFC 21 content on storage, nor is CFC 21 produced from fluoroplastics examined, nor is CFC 21 observable in CFC 11 or CFC 12 standards. CFC 21 is highly variable, and more measurements are needed.

Table 3 (continued)

Dr. R. A. RASMUSSEN -- Private -- 80-308. F-22 Measurements in the Atmosphere.

The concentration of CFC-22 is being measured in approximately 75 air samples collected since April 1978 by the ALE network with supplemental samples from late 1976. The data will be used to determine the rate of increase of CFC-22 over the past three years.

Dr. B. A. RIDLEY -- York University -- 76-102A, 76-102B. Measurement of Fluorocarbons and Related Chlorocarbons in the Stratosphere by Collection and Analysis (completed).

Series of evacuated stainless steel spheres were used to obtain samples of stratospheric air at various altitudes up to 39 km from three balloon flights. Some problems were encountered in the absolute calibration of the electron capture gas chromatograph, but the results are consistent with a stratospheric photolysis sink for CFC 11 and 12 and N_2O .

Drs. P. M. SOLOMON and R. L. deZAFRA -- State University of New York, Stony Brook -- 76-130, 77-225, 79-278, 80-316. Millimeter Wave Observations of Chlorofluoromethane Byproducts in the Stratosphere.

This study is directed toward the development of a ground-based method for continuous determination of ClO . One of the millimeter wave observing systems is based on a 3-nm maser, a unique instrument that is the most sensitive detector in the world in the 83-94 GHz range.

A 256-channel radio frequency spectrometer has been built and tested for the analysis and identification of the weak pressure-broadened 93 GHz signal from stratospheric ClO . An upper limit of 1.5 ppb ClO was measured with the 130 GHz receiver. In a joint effort with Bell Laboratories ClO has been detected at 201 GHz at an observatory near Amherst, Massachusetts.

In early 1980 the daily variability in the total ClO column was about a factor of 2, which is not predicted by the models. The average total ClO column was about a factor of 2 lower than model predictions. These measurements also indicate that the ClO in the lower stratosphere is less than the model profile, indicating that the OH concentration is also lower than calculated. These results imply a lower ozone depletion than now estimated.

Table 3 (continued)

Dr. O. C. TAYLOR -- University of California at Riverside -- 73-3, 74-2. Monitoring and Atmospheric Reactions of Fluorocarbons (completed).

An electron capture gas chromatograph was used to measure the concentrations of CFCs 11 and 12 in the troposphere over southern California and in the lower stratosphere over New Mexico and Colorado. The tropospheric concentrations were found to vary from day to day as climatic conditions affected dispersion and dilution. Concentration decreased with increasing altitude in the lower stratosphere.

Dr. R. A. YOUNG - Xonics, Inc. -- 75-50, 75-86. Development of an Instrument to Measure, O, ClO, O₃, and Total Cl in the Stratosphere (completed).

A preliminary evaluation of resonance fluorescence for the stratospheric measurement of ClO and total chlorine was made during the September 1975 STRATCOM balloon flight. This work and subsequent laboratory work indicated that alternative methods for these measurements hold greater near-term promise.

Dr. R. ZANDER -- University of Liege -- 76-141, 78-232. Ground-based Infrared Measurements.

The 7.5-meter focal length double-pass infrared spectrometer at the Jungfraujoch International Scientific Station (altitude 3580 meters) is being used to monitor atmospheric column densities of HF, HCl, and CH₃Cl in the 2-5 micron range. Resolution of the instrument is about 0.02 cm⁻¹. The equipment will also be modified to cover the 8-13 micron region to permit monitoring of HNO₃, CFCs 11 and 12, CCl₄, ClO, and ClONO₂.

Results indicate a steady increase of about 10% per year in HF content in the stratosphere, whereas there is no clear trend in the average column density of HCl.

Average column mixing ratios of $1.5 \pm 0.6 \times 10^{-9}$ for CH₃Cl in June 1979 and an upper limit of $1.5 \pm 0.5 \times 10^{-10}$ for ClONO₂ were measured. Cloud cover limited winter measurements.

Table 3 (continued)

E. Modeling

Dr. G. BRASSEUR -- Institut d'Aeronomie Spatiale,
Belgium -- 80-320. Modeling of the CFC Effect on
the Ozone Layer.

A 2-D model will be developed in which the chemistry is coupled with dynamics and temperature distribution. A 1-D model will be used for studying new chemistry. Special emphasis will be given to comparison between observed and computed distributions of trace species (N_2O , CFC-11, CFC-12, CH_4 , ClO ,) and studies of simultaneous perturbations (e.g., CFCs and CO_2) including thermal and dynamical feedbacks on perturbation calculations.

Drs. D. M. CUNNOLD, F. N. ALYEA, and R. G. PRINN --
CAP Associates -- 75-24, 76-122, 77-199, 78-252, 79-281,
80-323. Meteorological and Multi-Dimensional Model-
ing Considerations Relating to Atmospheric Effects
of Halocarbons.

Studies to assess the accuracy and shortcomings of the 1-D model used to estimate ozone depletion indicated that a tropospheric lifetime for CFCs 11 and 12 as short as 10 years was not inconsistent with atmospheric measurements. Thus, ozone depletion estimates might be considerably less than present estimates. The great variability of stratospheric measurements indicates that simultaneous measurements for many important stratospheric species are needed and that seasonal dependence of species must be considered.

The neglect of dynamical feedback processes in the radiative models used to calculate warming (greenhouse effect) limits the value of calculated effects. Preliminary calculations have been made including feedback effects due to inclusion of the hydrological cycle and circulatory effects. Preliminary results indicate that inclusion of the hydrological cycle would strongly counteract the greenhouse effect, whereas circulatory changes would slightly increase it.

Because it has been shown that meteorological conditions can cause variations in both tropospheric and lower stratospheric fluorocarbon measurements in Alaska, temporal and latitudinal variability of fluorocarbon concentration has been estimated with the use of an 8-box model of the troposphere, and the results related to the sensitivity of trend detection in the Atmospheric Lifetime Experiment (cf. 79-281, p. 17) and to previous interhemispheric observations.

A preliminary estimate was made for the lifetime of a tropospheric sink due to photodecomposition of CFCs on sand. The sink would imply a lifetime of 30 years if 40% of the CFCs were destroyed over the Sahara Desert.

Table 3 (continued)

A methodology was developed for determining the lifetime of tropospheric sinks of CFCs by daily monitoring. This methodology is being implemented under 79-279, 79-280 and 79-281 (pp. 21, 19, and 17, respectively).

The surface temperature increase resulting from atmospheric CFC mixing ratios increasing to 2 ppbv has been reestimated at $0.2 \pm 0.5^\circ\text{K}$ (95% confidence limits). The significance of its impact is thus extremely uncertain and is only one of a number of factors that could induce climatic change.

Dr. N. D. SZE -- Environmental Research and Technology, Inc. -- 75-32, 76-115. Model Analysis of The Fluorocarbon Problem (completed).

A one-dimensional model has been used to evaluate the role of stratospheric water in the NO_x and Cl_x cycles, the relationship of eddy diffusion coefficient and CFC lifetime, the use of CFC measurements to calculate lifetime, and the effect of chlorine nitrate. The importance of OH concentration on calculated ozone depletion was shown, and key reactions were identified. Analyses showed 10-20 year tropospheric lifetimes were not inconsistent with measurements and helped to define quantitatively the uncertainties associated with ozone depletion calculations.

Inclusion of multiple scattering in the model had a negligible effect on the ozone depletion estimates. The modeled ozone profile above 40 km is a factor of 2-3 lower than recent measurements. Calculated ClO profiles are a factor of 2-4 too low at 28-35 km when compared with Anderson's ClO data.

A diurnal model has been developed that is capable of calculating stratospheric concentration profiles of any HO_x , ClO_x , or O_x species.

Dr. N. D. SZE -- Atmospheric & Environmental Research Inc. -- 77-173, 78-234, 79-273, 80-311. Theoretical Models of Stratospheric Chemistry, Perturbations, and Trace Gas Measurements (continuation of 76-115).

Iterative procedures, which lower the computer time by a factor of 3 for the diurnal model, have been developed.

The modeled HF data and HF/HCl ratio are at least a factor of 2 higher than the measured values. A possible explanation is that OH is less than model predictions, thus indicating a greater reservoir of inactive chlorine. If the rate of formation of OClO is sufficiently rapid, it can constitute a "holding tank" for active chlorine.

Theoretical calculations indicate that the possibility of a 20-year tropospheric sink due to adsorption of CFCs 11 and 12 on desert sand with subsequent photodecomposition by sunlight cannot be ruled out.

Table 3 (continued)

Incorporating new rate constants for the reactions $\text{HO}_2 + \text{NO} \rightarrow \text{NO} + \text{NO}_2$ and $\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$ raises calculated steady state ozone reduction to a level that should be detectable within 6-8 years using an 18-station network of ozone monitoring stations.

It has been shown that if 10% of the reaction between HO_2 and ClO proceeds by the product channel $\text{HCl} + \text{O}_3$ the ozone depletion estimate can be lowered by a factor of at least 2.

Preliminary work on 2-D models has utilized a simplified compartmental approach. Spatial inhomogeneity of effects is predicted. A full 2-D model has been developed in a joint effort with the U. S. Air Force.

Preliminary indications are that if the downward eddy diffusion coefficient is larger than the upward eddy diffusion coefficient, then the calculated ozone reduction due to release of CFCs would be reduced. Also, a preliminary analysis shows that the total ozone column is sensitive to the eddy diffusion coefficient. This could have a potential feedback effect on the ozone depletion estimate if the eddy diffusion coefficient changes with changes in ozone.

Studies on the effect of coupling the perturbations to the atmosphere due to increased concentrations of CO and CH_4 and increased use of fertilizer show that the net perturbation of ozone may be significantly less than for CFCs alone. In particular, it has been shown that coupling the effects due to increasing CO_2 resulting from greater use of fossil fuel and CFC emissions results in a lower value for the ozone depletion estimate.

The effect of anthropogenic and natural emissions of organic bromine compounds has been considered in the model and found to have a minimal effect on the ozone depletion estimate. The potential importance of $\text{O}_2(^1\Delta_g)$ reactions has been shown. Introduction of this chemistry along with the measured $\text{O}_2(^1\Delta_g)$ profile into the model could enhance the $\text{O}-\text{O}_3$ ratio and magnify existing discrepancies between measured and modeled profiles.

Current values of photodissociation cross sections for HO_2NO_2 indicate that its reaction with HO could result in a reduction of the ozone depletion estimates and in better agreement between measured and calculated profiles for many atmospheric species. Measurement of C_2H_6 and C_2H_2 can be used to infer local concentrations of HO and Cl , a further check on observed and calculated profiles.

Using current values for the rate constants for the reactions of HO with HO_2 , HNO_3 , and OH lowers ozone depletion estimates by about a factor of 2.

Table 3 (continued)

F. Other

Dr. M. J. BAILEY -- University of Maryland -- 80-317
Uncertainties and Benefit-Cost Analysis of CFC Control.

A recently concluded, EPA-funded analysis of the potential costs and benefits of CFC control is being expanded and further refined. The new study takes into account recent revisions in atmospheric models and projected future changes in atmospheric composition. Although the range of possible outcomes is broad, indications for the most likely case are that the benefits of unregulated fluorocarbon use will outweigh any of their harmful effects.

Dr. D. BERGER -- Temple University -- 75-62. Ground-Level Monitoring of Ultraviolet Solar Radiation (completed).

The monitoring of solar ultraviolet radiation, which was initiated by the Climatic Impact Assessment Program (CIAP) and subsequently funded for one year by CMA, is now being supported by NOAA.

Drs. E. PARZEN and M. PAGANO -- Frontier Science and Technology Research Foundation, Inc. -- 76-106. Total World Ozone Level: Statistical Analysis (completed).

Ozone column measurements from at least 20 stations have been evaluated statistically to detect trends in recorded ozone concentrations and to establish the limits of detection for such trends. Time series analysis has been shown to be substantially more sensitive in detecting non-random ozone changes than the estimates of such sensitivity made by the Federal Task Force on Inadvertent Modifications of the Stratosphere (IMOS) in 1975. Analysis of ozone data from 9 stations shows that no detectable abnormal trend in the ozone data has occurred over the last 6 years. The absence of detectable trends provides an upper limit for actual depletion and a test of model predictions.

If sufficient sensitivity is achieved, this technique will enable an effective early warning system for ozone depletion to be established.

Drs. G. C. TIAO and G. REINSEL -- University of Wisconsin -- 78-250, 80-304. Statistical Analysis of World-wide Stratospheric Ozone Data for the Detection of Trend.

The ground-based and satellite ozone data are being obtained and prepared in a form suitable for computer analysis. Analysis of long-term ozone data from 36 ground-based stations shows an average increase of $0.3\% \pm 1.4\%$ for the period 1970-1978. The NAS report indicates that the ozone should have decreased by

Table 3 (continued)

1.5% \pm 1.1% during that same period. The difference between these two studies is statistically significant. Ground-based data are currently being compared with satellite ozone data in order to assess the magnitude of errors due to instrument drift and non-uniform positioning of ground-based ozone-measuring stations. In addition, efforts to correlate long-term meteorological variables with ozone data, in order to assess whether there are long-term cycles in the ozone data, are in progress.

Dr. G. S. WATSON -- Princeton University -- 78-257.
Statistical Investigations of the CFM Problem.

Available data on ozone and related variables are being studied in an attempt to understand the natural variation of ozone in space and time. Theoretical models for ozone trends and their predictions are being checked against observed ozone as a function of time and position. An effective "early warning" system will then be designed.

Preliminary analysis of Umkehr data from 32-50 km, where maximum ozone depletion is predicted, has shown a slight increase in ozone. The models predict a 5% decrease.

Table 3 (continued)

G. Consultants

1. Under Contract

Dr. J. G. Anderson	Harvard University	Stratospheric Measurements
Dr. A. W. Castleman, Jr.	University of Colorado	Heterogeneous Chemistry
Dr. D. R. Herschbach	Harvard University	Homogeneous Chemistry, Kinetics, and Spectroscopy
Dr. I. C. Hisatsune	Pennsylvania State University	Molecular Spectroscopy and Chemical Kinetics
Dr. L. E. Snyder	University of Illinois	Millimeter Wavelength Spectroscopy
Dr. R. T. Watson	Jet Propulsion Laboratory	Chemical Kinetics and Photochemistry

2. Without Compensation

Dr. F. C. Fehsenfeld	} NOAA Environmental Research Laboratories	Reactions of Charged Species
Dr. E. E. Ferguson		

November 30, 1980

Table 4A

Research Funded by the Chlorofluorocarbon Industry

and

Administered by the Chemical Manufacturers Association

WORK COMPLETED

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Investigation of spectroscopy of and photochemical changes in fluorocarbons	Sandorfy	U. of Montreal	73-2	10/11/74
Monitoring of fluorocarbons in the atmosphere and simulation of atmospheric reactions of fluorocarbons ^b	Taylor	U. of Calif.- Riverside	73-3	10/16/74
Measurement of fluorocarbons in the atmosphere ^b	Lovelock	U. of Reading	73-1	10/27/74
Laboratory investigation of the feasibility of measuring ClO in the atmosphere by the chemical conversion-resonance fluorescence detection method	Stedman	U. of Michigan	74-7	2/28/75
Laboratory determination of sensitivity of laser-induced fluorescence for the detection of ClO under atmospheric conditions	Davis	U. of Maryland	74-10	5/31/75
Continuation of 73-3 ^b	Pitts	U. of Calif.- Riverside	74-2	12/31/75
Continuation of 73-1 ^b	Lovelock	U. of Reading	74-3	12/31/75
Investigation of ion-molecule reactions involving chlorofluorocarbons	Mohnen	SUNY-Albany	75-64	4/1/76
Development of an instrument to measure O, ClO, O ₃ , and total Cl in the stratosphere ^b	Young	Xonics, Inc.	75-50	4/7/76

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Measurement of fluorocarbons and related chlorocarbons in the stratosphere and upper troposphere ^b	Rasmussen	Washington State U.	75-2	4/15/76
Continuation of 74-2	Pitts	U. of Calif.- Riverside	75-12	4/15/76
Investigation of the destruction of chlorofluoromethanes by naturally occurring ions	Campbell	Washington State U.	75-53	4/23/76
Ground-based millimeter wavelength observations of stratospheric ClO	Ekstrom	Battelle Northwest	75-27	5/24/76
Laboratory and theoretical studies of the ultraviolet and visible electronic spectra of ClO ^b	Nicholls	York U.	75-11	6/14/76
Modeling of the fluorocarbon-ozone system ^b	Sze	ERT, Inc.	75-32	8/18/76
Critique of models used to estimate chlorofluorocarbon effects on ozone ^b	Cunnold, Alyea, Prinn	CAP Associates	75-24	9/10/76
Studies of reactions of HO ₂ by laser magnetic resonance	Thrush	U. of Cambridge	75-58	11/8/76
Continuation of 75-50	Young	Xonics, Inc.	75-86	11/15/76
Measurement of stratospheric distribution of fluorocarbons and related species by infrared absorption spectroscopy ^b	Murcray	U. of Denver	75-13	1/24/77
Measurement of reaction rates relevant to the fluorocarbon-ozone problem ^b	Birks	U. of Illinois	75-1	2/4/77
Measurement of OH in the stratosphere by laser induced fluorescence	Davis	U. of Maryland	75-87	2/23/77

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Exploration for unidentified factors in the fluorocarbon-ozone problem ^b	Lovelock	Private	75-67	3/10/77
Laboratory studies of the infrared vibration-rotation spectrum of ClO	Nicholls	York U.	75-30b	3/25/77
Absolute calibration of fluoro-carbon measurements	Stedman	U. of Michigan	76-132	4/1/77
Collection and analysis of Antarctic ice cores	Rasmussen	Rasmussen Assoc.	75-84	4/19/77
The electron capture detector as a reference standard in the analysis of atmospheric halocarbons	Lovelock	Private	76-120	5/3/77
Laboratory measurement of spectroscopic absorption cross sections of ClO	Davis	U. of Maryland	75-73	5/12/77
Measurement of fluorocarbon content of "antique" air samples	Rasmussen	Washington State U.	75-71	9/2/77
Measurement of HCl and HF in the stratosphere by Fourier transform spectroscopy ^b	Buijs	Bomem, Inc.	75-98	9/26/77
Continuation of program for ground level monitoring of ultraviolet solar radiation	Berger	Temple U.	75-62	10/20/77
Continuation of 75-1 ^b	Birks	U. of Illinois	76-117A	12/12/77
Studies of heterogeneous reactions ^b	Birks	U. of Illinois	76-117B	12/12/77
Meteorological and multi-dimensional modeling considerations relating to atmospheric effects of halocarbons ^b	Cunnold, Alyea, Prinn	CAP Associates	76-122	12/12/77
Climatic effects of fluoro-carbons ^b	Cunnold, Alyea, Prinn	CAP Associates	76-122S	12/12/77

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Electron spin resonance detection of stratospheric radicals	Ehhalt	Nuclear Research Establishment - Juelich	76-145	12/12/77
Measurement of the concentration of methyl chloride in air in Kenya	Rasmussen	Private	77-181	12/12/77
Continuation of 75-67 ^b	Lovelock	Private	77-144	12/23/77
Kilauea volcanic emissions--halocarbon measurement	Rasmussen	Oregon Graduate Center	77-215	12/27/77
Laboratory determination of the feasibility of laser magnetic resonance for ClO detection and reaction studies	Howard	NOAA-Boulder	75-47	1/10/78
Photochemical and chemical kinetic measurements of stratospheric importance with respect to the fluorocarbon issue ^b	Timmons	Catholic U.	76-129	1/16/78
Laboratory measurement of high resolution infrared spectra of chlorine-containing molecules of stratospheric interest ^b	Murcay	U. of Denver	75-92	2/10/78
Reactions of the HO ₂ radical studied by laser magnetic resonance	Thrush	U. of Cambridge	75-58 II	3/2/78
Construction of Fourier-transform spectrometer	Buijs	Bomem, Inc.	75-90	3/8/78
Interlaboratory comparisons of fluorocarbon measurements ^b	Rasmussen	Private	76-142	3/8/78
Generation and exchange of calibrated samples of fluorocarbons	Stedman	U. of Michigan	77-151	3/10/78
Laboratory investigation of the heterogeneous interaction of Cl and ClO with H ₂ SO ₄ ^b	Martin	Aerospace Corp.	75-81	3/27/78

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Continuation of 75-32 ^b	Sze	ERT, Inc.	76-115	3/28/78
Studies of compounds of sulfur, oxygen, and chlorine ^b	Kaufman	Emory U.	76-126	5/24/78
Total world ozone level: statistical analysis	Parzen, Pagano	Frontier Science and Technology Research Foundation, Inc.	76-106	5/25/78
Stratospheric measurement of ClO and OH	Murcray	U. of Denver	76-135	5/30/78
Laboratory study of the UV and IR spectra of HOCl, HOONO ₂ , and HClO ₄ in the temperature range of the stratosphere	Knauth	U. of Kiel	77-171	6/14/78
Photochemistry of small chlorinated molecules ^b	Wiesenfeld	Cornell U.	76-128	7/5/78
Continuation of 75-2	Rasmussen	Washington State U.	75-59	8/10/78
Atmospheric chemistry of peroxyntitric acid	Pitts	U. of Calif.-Riverside	77-190	11/13/78
Continuation of 75-81	Martin	Aerospace Corp.	75-81 II	12/6/78
Ground-based infrared measurements ^b	Zander	U. of Liege	76-141	12/11/78
Measurements of HCl, HF, ClO, etc., in the stratosphere by high resolution infrared spectroscopy	Girard	ONERA-France	75-88	1/2/79
Coordination and analysis of data for atmospheric life-time experiment ^b	Cunnold, Alyea, Prinn	CAP Associates	77-213	2/13/79
Measurement of fluorocarbons and related chlorocarbons in the stratosphere by collection and analysis	Ridley	York U.	76-102	2/26/79
Continuation of 76-122 ^b	Cunnold, Alyea, Prinn	CAP Associates	77-199	2/26/79

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Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Operation of stations at Adrigole and Barbados for atmospheric lifetime experiment ^b	Lovelock, Simmonds	Private	77-193	2/28/79
Operation of stations in American Samoa and Tasmania for atmospheric lifetime experiment ^b	Rasmussen	Oregon Graduate	77-201	3/29/79
Development of primary fluoro-carbon standards	Lovelock	Private	78-226	4/2/79
Experimental investigation of the branching ratio in the $O(^1D) + H_2O$ reaction	Zellner	U. of Goettingen	77-195	4/12/79
Acquisition of on-board digital recording system	Murcay	U. of Denver	77-211	4/12/79
Theoretical models of stratospheric chemistry, perturbations, and trace gas measurements ^b	Sze	AER, Inc.	77-173	4/17/79
Determination of the photodissociation process and absorption cross section of FC-11 and 12 in the near UV	Stuhl	U. of Bochum	77-170	5/3/79
Continuation of 76-129 ^b	Timmons	U. of Texas-Arlington	77-214	6/15/79
Total chlorine measurements in the troposphere and stratosphere	Eggleton	AERE Harwell	76-116	7/6/79
Millimeter wave observations of chlorofluoromethane byproducts in the stratosphere ^b	Solomon, deZafra	SUNY Stony Brook	76-130	7/6/79
Continuation of 76-126	Kaufman	Emory U.	77-197	7/6/79
Photoabsorption cross sections for compounds of atmospheric interest	Takacs	Rochester Inst. Technol.	77-196	7/24/79

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Lower stratospheric measurement of non-methane hydrocarbons	Rasmussen	Private	76-140	7/30/79
Laboratory study for determination of the equilibrium constant of the reaction $\text{Cl}_2\text{O} + \text{H}_2\text{O} = 2 \text{HOCl}$ and the UV spectrum of HOCl	Knauth	U. of Kiel	77-224	8/9/79
Effect of aerosol scattering on ozone measurements with the Dobson spectrophotometer	Moe	Private	78-235	9/12/79
Continuation of 75-92 ^b	Murcra y	U. of Denver	77-152	10/17/79
Studies of homogeneous and heterogeneous reactions of importance to the stratosphere ^b	Birks	U. of Colorado	77-192	11/8/79
Photodegradation of chlorofluoromethane in the troposphere	Korte	U. of Munich	77-194	11/16/79
Follow-up for photodecomposition of chloromethanes absorbed on silica surfaces ^b	Ausloos	NBS	77-186	11/28/79
Continuation of 77-213 ^b	Cunnold, Alyea, Prinn	CAP Associates	78-251	12/17/79
Continuation of 77-199 ^b	Cunnold, Alyea, Prinn	CAP Associates	78-252	1/18/80
Continuation of 76-128	Wiesenfeld	Cornell	77-220	2/1/80
Measurement of halogen compounds for determination of total chlorine and total fluorine in the stratosphere using long-path interferometric spectroscopy	Buijs	Bomem, Inc.	77-168	2/4/80

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Determination of a measurement system for the determination of total chlorine in air	Skogerboe	Colorado State U.	77-206	2/4/80
Identification of FC 21 in the atmosphere	Rasmussen	Oregon Graduate Center	78-260	2/5/80
Continuation of 76-130 ^b	Solomon, deZafra	SUNY Stony Brook	77-225	2/13/80
Continuation of 77-193 ^b	Lovelock, Simmonds	Private	78-243	2/18/80
Continuation of 77-192 ^b	Birks	U. of Colorado	78-244	2/20/80
Laser magnetic resonance study of HO ₂ chemistry	Howard	NOAA-Boulder	76-100	3/12/80
Study of ClO chemistry by laser magnetic resonance	Howard	NOAA-Boulder	77-223	3/12/80
Continuation of 77-201 ^b	Rasmussen	Oregon Graduate Center	78-248	4/24/80
Development and implementation of a simplified multidimension model for stratospheric chemistry perturbations, radiation feedback and trace gas measurement ^b	Sze	AER, Inc.	78-234	5/14/80
Continuation of 77-142	Rasmussen	Oregon Graduate Center	78-247	5/28/80
Detection of selected molecules by ground-based solar spectroscopy	Murcray	U. of Denver	78-228	5/29/80
Analysis of Release of FC-11 from Rigid Plastic Foam Products in the U. S.	Shamel	A.D.Little, Inc.	79-275	5/29/80
The exponential dilution chamber for the calibration of instruments and the preparation of standards ^b	Lovelock	Private	78-264	7/9/80

(continued)

Table 4A (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Completion Date</u>
Rates of reaction of Cl atoms with the primary products of alkane photooxidation	Kurylo	NBS	78-233	9/4/80
Determination of FC-21 and other halocarbons in the troposphere	Bruner	Urbino U.	78-256	9/23/80
Determination of atomic oxygen yields in the photolysis of HOCl and ClOO	Phillips	U. of Canterbury (N.Z.)	78-241	9/30/80
Submillimeter-infrared balloon experiment ^b	Bonetti, Carli, Harries	CNR - IROE (Florence, Italy), National Physiscal Laboratory U. K.	76-137	11/6/80
Effectiveness of various untreated sand surfaces bringing about the oxidation of CCl ₄ , CFC ₁₃ , and CF ₂ Cl ₂	Ausloos	NBS	78-254	c
The A ² Π ₁ + X ² Π ₁ Band System of ClO ^b	Coxon	Dalhousie U.	78-255	c

a. Abbreviated affiliations are expanded under study descriptions in Table 3.

b. Work continued in a follow-on contract.

c. Final report accepted by the Panel.

November 30, 1980

Table 4B

Research Funded by the Chlorofluorocarbon Industry

and

Administered by the Chemical Manufacturers Association

WORK IN PROGRESS

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Contract Date</u>	<u>Contract Period</u>
Continuation of 75-13	Murcray	U. of Denver	76-101	4/6/76	12 mo. ^b
Continuation of 75-11	Nicholls	York U.	75-11 II	8/18/76	12 mo. ^b
Operational costs for flights planned in 1977	Buijs	Bomem, Inc.	77-156	6/9/77	12 mo. ^b
Laboratory measurment of infrared spectra of selected stable molecules	Buijs	Bomem, Inc.	77-221	2/24/78	14 mo. ^b
Development of technique for measuring total chlorine content of air	Howard, Birks, Fehsenfeld	NOAA-Boulder/ U. of Colorado	77-222	3/27/78	12 mo. ^b
Simultaneous balloon flight with J. G. Anderson	Murcray	U. of Denver	77-166	4/27/78	9 mo. ^b
Continuation of 76-141	Zander	U. of Liege	78-232	6/28/78	12 mo. ^b
Absorption measurements of HOCl and related molecules	Timmons	U. of Texas-Arlington	78-258	1/12/79	12 mo. ^b
Statistical analysis of worldwide stratospheric ozone data for the detection of trends ^c	Tiao, Box	U. of Wisconsin	78-250	4/4/79	18 mo. ^b
Continuation of 78-234 ^c	Sze	AER, Inc.	79-273	7/26/79	12 mo. ^b
Statistical investigations of the CFM problem	Watson	Princeton U.	78-257	8/2/79	24 mo.
Continuation of 77-152	Murcray	U. of Denver	78-265	8/23/79	12 mo. ^b
Continuation of 78-244 ^c	Birks	U. of Colorado	79-276	9/1/79	12 mo. ^b

(continued)

Table 4B (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Contract Date</u>	<u>Contract Period</u>
Combination and continuation of 78-251 and 78-252 ^c	Cunnold, Alyea, Prinn	CAP Assoc.	79-281	11/16/79	12 mo. ^b
Determination of tropospheric halocarbons and their relative importance	Simmonds, Lovelock	Private	79-269	11/19/79	12 mo. ^b
Continuation of 78-243 ^c	Simmonds	Private	79-280	11/20/79	12 mo. ^b
Operation of Fifth ALE Station, Cape Meares, OR ^c	Rasmussen	Oregon Graduate Center	78-263	11/21/79	12 mo. ^b
Continuation of 78-248 ^c	Rasmussen	Oregon Graduate Center	79-279	11/21/79	12 mo. ^b
Continuation of 77-225 ^c	Solomon, deZafra	SUNY Stony Brook	79-278	1/3/80	12 mo.
Reaction of ClO with OH	Donovan	U. of Edinburgh	79-286	2/20/80	12 mo.
Kinetic Studies of Stratospheric Chlorine Chemistry	Howard	NOAA-Boulder	79-289	4/20/80	12 mo.
Reaction of OH with ClO	Ravishankara	Georgia Tech.	80-295	5/23/80	12 mo.
Continuation of 78-264	Lovelock	Private	80-293	6/9/80	6 mo.
Airborne millimeter wave determination of ClO	Beckman	Queen Mary College, London	79-282	6/24/80	6 mo.
Uncertainties and benefit-cost analysis of CFC control	Bailey	U. of Maryland	80-317	8/7/80	Open
Continuation of 79-273	Sze	AER, Inc.	80-311	8/11/80	12 mo.
Continuation of 79-278	Solomon, deZafra	SUNY Stony Brook	80-316	8/19/80	12 mo.
Measurement of the Vertical Distribution of HCl, O ₃ , and HCHO and the ratio HF/HCl	Jouve	U. of Reims	79-290	9/18/80	12 mo.

(continued)

Table 4B (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Contract Date</u>	<u>Contract Period</u>
F-22 measurements in the atmosphere	Rasmussen	Private	80-308	9/26/80	6 mo.
Continuation of 78-250	Reinsel, Tiao	U. of Wisconsin	80-304	10/13/80	15 mo.
Continuation of 79-276	Birks	U. of Colorado	80-321	10/21/80	12 mo.
Continuation of 78-255	Coxon	Dalhousie U.	80-315	10/23/80	12 mo.
Far-infrared laboratory spectroscopy of halogen-containing molecules	Traub, Chance	Smithsonian Astrophysical Observatory at Harvard	80-318	10/31/80	12 mo.
Continuation of 79-281	Cunnold, Alyea, Prinn	CAP Assoc.	80-323	11/18/80	12 mo.
Continuation of 76-137	Bonetti	U. of Florence	80-297	Pending	12 mo.
Infrared spectroscopy of atmospheric species	Howard	NOAA-Boulder	80-299	Pending ^d	12 mo.
Near- and Far-Infrared Spectroscopy	Saykally	U. of California	80-300	Pending	24 mo.
Reactions within the HO _x cycle	Kurylo	NBS	80-307	Pending	12 mo.
Modeling of the CFC effect on the ozone layer	Brasseur	Institut d'Aeronomie Spatiale, Belgium	80-320	Pending	12 mo.
Collaborative studies on atmospheric spectroscopy	Goldman, Barbe	U. of Denver/ U. of Reims	80-322	Pending	12 mo.
Continuation of 79-280	Simmonds	Private	80-324	Pending	12 mo.
Continuation of 78-263 and 79-279	Rasmussen	Oregon Graduate Center	80-325	Pending	12 mo.
An intercomparison of measurements of stratospheric HCl	Murcray, Roscoe	U. of Denver, Oxford U.	80-328	Pending	Open

(continued)

Table 4B (continued)

<u>Program</u>	<u>Investigator</u>	<u>Organization^a</u>	<u>Proposal Number</u>	<u>Contract Date</u>	<u>Contract Period</u>
Continuation of 79-276	Birks	U. of Colorado	80-329	Pending	12 mo.

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- a. Abbreviated affiliations are expanded under study descriptions in Table 3.
 - b. Contract extended.
 - c. Work continued in a follow-on contract.
 - d. Dependent on appropriate cofunding.

November 30, 1980

Table 5

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1. Simultaneous Measurement of the Volume Mixing Ratios of HCl and HF in the Stratosphere, H.L.B., G.L. Vail, G. Tremblay, and D.J.W. Kendall, Geophys. Res. Lett., 7 (3), 205-8 (1980).

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"	77-214 (c)	29
"	78-258	29
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* (c) indicates completed project

X. APPENDIX L

UNCERTAINTIES - CHLOROFLUOROCARBON EFFECTS
AND STRATOSPHERIC OZONE
(SRI REPORT)

Uncertainties

The following Appendix is taken from a report [SRI, 1980] of a March, 1980 workshop run by SRI International for the EPA. The workshop was sponsored by EPA to evaluate "...the critical issues that are hindering EPA's ability to make a fully supportable decision on further CFC regulations." The principle findings of the workshop are summarized in the report's Table 2 (attached). The full report also is included as part of the Du Pont submission.

TABLE 2. IMPORTANT ISSUES IN CHLOROFLUOROCARBON EFFECTS AND OZONE DEPLETION

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e	<u>Uncertainties</u>
High	Releases	Identify what chemicals are likely to deplete ozone or affect near-surface temperatures, and thus should be assessed as to their current and future releases.	Yes	1	
		Describe how patterns of technological innovation will change the need for CFCs and related substances and create new policy options not currently under consideration for CFC control.	Yes, with difficulty	2-5	
		Improve accuracy of projections of future U.S. emissions by CFCs, by source, under the assumption of no further regulatory interventions.	Yes	2	
High	Transport and Chemistry	Validate models of ozone depletion against measurements, with calibration as required; may be direct measurement of ozone or measurements of ratios of species.	Yes	5	
High	Climate	Describe spatial and temporal variations in temperature, precipitation, cloudiness, and evapotranspiration, leading to description of changes in soil moisture.	Yes	10	
		Estimate synergistic effects of CFCs with CO ₂ on temperature change, because increments are more likely to be adverse if baseline is significantly disturbed.	Yes, but not under EPA program	2-5	

TABLE 2. (Continued)

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e
High	Health	Integrate by epidemiology the form of the relationship of melanoma incidence and mortality of ultraviolet exposures over the range possible from CFC releases.	Yes	2-5
High	Biology/ Ecology	Obtain and evaluate available data on the patterns of habits and habitats of aquatic species that determine their exposure and susceptibility to ultraviolet light.	Yes	1-2
		Determine and explain the differences between laboratory and field susceptibility to ultraviolet radiation of selected crops and aquatic species.	Yes	2
		Determine the environmental and health consequences of proposed substitutes for CFCs.	Yes	2
High	Economics	Develop a combined scientific and ethical basis for setting discount rates for estimates of future control costs and benefits, including different rates for costs and benefits if necessary.	Yes	2
		Determine the social value placed on the responsibility to future generations and the way to treat potential catastrophic effects.	Yes	1
		Describe the proper way to evaluate the significance of changes (such as a large change in average atmospheric ozone content) never before experienced, and how society should respond to them.	No	

Uncertainties

TABLE 2. (Continued)

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e	<u>Uncertainties</u>
Moderate	Releases	Improve estimates of current and future release rates outside the United States under the assumption of no further regulations.	Yes	1-2	
		Determine what U.S. government policy will be on other issues, such as solvent use of non-CFCs.	No		
		Estimate the worldwide elasticity of demand to CFC prices so that the response of industry to various policy interventions can be understood better.	Yes	2-5	
		Determine release rates of other pollutants that either deplete ozone or affect the transport and chemistry of ozone-depletors.	Yes	2	
Moderate	Transport and Chemistry	Model and measure how CFCs selectively change the temporal and spatial variations in ozone concentrations: Are variations damped or accentuated?	Yes	5-10	
		Determine the influence of other man-made and natural emissions on the effectiveness of CFC ozone depletion.	Yes	1-3	
		Set upper bounds on the effectiveness of possible tropospheric processes that destroy or entrap CFCs and thus reduce their flux to the stratosphere.	Yes	5	
		Investigate the adequacies of one-dimensional and multi-dimensional models in describing average and spatially resolved ozone depletion.	Yes	5-10	

TABLE 2. (Continued)

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e
Moderate	Climate	Identify additional chemical species that can significantly affect the global temperature balance and estimate their effects.	Yes	2
		Refine our understanding of the global feedback parameter that accounts for water vapor in the atmosphere, albedo of clouds and surface, vertical temperature profile and so on to determine the temperature change equivalent to a given heat input change.	Yes	5
		Improve knowledge of temperature changes in the stratosphere and consequences on weather.	Yes	5-10
Moderate	Health	Develop a biological model (experimental animal study) for examining the melanoma dose-response relationship, and explore the theoretical biology implied.	Yes	5-10
		Investigate the dependence of non-melanoma and especially melanoma cancer incidence on dose-rate, especially for very high short-term exposures.	Yes	10
		Determine whether an average increase in UV will push the natural variations in UV over a biological stability level for melanoma.	Not in reasonable time	
		Separate the effects of UV irradiation from other causative factors, especially for melanoma.	Yes	2-5
		Establish and explain the relationship of non-melanoma skin cancer incidence to ultraviolet exposures over the range possible from CFC releases.	Yes	2-5

Uncertainties

TABLE 2. (Continued)

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e
Moderate	Health	Determine the population distribution of UV doses by geography, time, and demographic characteristics.	Yes	3
		Describe the likely human behavioral response to increased levels of UV and (possibly) temperature.	Yes	2
Moderate	Biology/ Ecology	Describe the variability of chlorophyll (a) distribution in natural waters and its effect on the penetration of UV with depth.	Yes	1
		Determine the significance of shifts in ecological community structure to the welfare and stability of the human environment.	Not in reasonable time	
		Estimate the susceptibility of sensitive environments (e.g., desert, tundra) to UV increase in comparison with more robust environments.	Yes	1-2
		Investigate the dependence of biological and ecological effects on UV dose rates, especially to understand the significance of experiments performed at high rates.	Yes	2-5
		Determine sensitivity of specific economically important crops to UV in the laboratory and in the field.	Yes	2
		Determine sensitivity of specific crops to temperature changes.	Yes	2
		Determine sensitivity of specific aquatic organisms to UV.	Yes	2

Uncertainties

TABLE 2. (Concluded)

Importance ^a	Area ^b	Issue or Uncertainty ^c	Researchable? ^d	Time (years) ^e
Moderate	Biology/ Ecology	Investigate the UV action spectra for selected biological effects.	Yes	3
		Determine likely adaptation of important species to increased UV.	Yes	10
Moderate	Economics	Describe what kinds of control decisions are, in practical terms, irreversible, and the social consequences of making erroneous ones.	Probably not	
		Develop methods for achieving equity given a distribution of costs and benefits to various parties, nationally or worldwide, over time.	No	
		Predict social behavior in response to the adverse consequences of UV and temperature change: Will society adapt to minimize their severity?	Yes	10

^aAn integrated subjective assessment of the importance of resolving the issue for decisions on CFC control. Both importance within the area of study and importance of the area to the decision are included. No significance is implied by the order within importance categories.

^bThe issues are roughly sorted by the area of study, but many are transdisciplinary.

^cThese descriptions are necessarily brief and may omit important subtleties. See also Section 5.

^dThis judgment depends both on the length of time required for meaningful progress and the likelihood of acceptance of the findings.

^eRange of time required to make significant progress in resolving the issue or reducing the uncertainty.

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