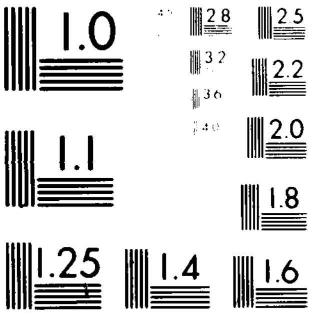
AD-A089 100 CENTER FOR THE ENVIRONMENT AND MAN INC HARTFORD CONN F/G 4/1
THE PERTURBATION OF SOME ATMOSPHERIC MECHANISMS BY EMISSIONS FR--ETC(U)
NOV 79 G D ROBINSON DOT-FA77WA-4055
UNCLASSIFIED CEM-4232-667 FAA/EE-80-16 NL

1 OF 2
AD
A089100


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

Report ~~No.~~ FAA-EE-80-16

(12) SR

THE PERTURBATION OF SOME ATMOSPHERIC MECHANISMS BY EMISSIONS FROM AIRCRAFT

G.D. Robinson
Principal Investigator

November 1979

FINAL REPORT

Prepared for

HIGH ALTITUDE POLLUTION PROGRAM

U.S. DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION
Office of Environment and Energy
Washington, D.C. 20591

(11)

Technical Report Documentation Page

1. Report No. (1) FAA-EE-80-16	2. Government Accession No. AD-A089 100	3. Recipient's Catalog No.
4. Title and Subtitle The Perturbation of Some Atmospheric Mechanisms by Emissions from Aircraft		5. Report Date November 1979 6. Performing Organization Code
7. Author(s) (10) G.D. Robinson Principal Investigator		8. Performing Organization Report No. (14) CEM-4232-667
9. Performing Organization Name and Address The Center for the Environment and Man, Inc. 275 Windsor Street Hartford, Conneticut 06120		10. Work Unit No. (TRAIS) 11. Contract or Grant No. (15) DOT-FA77WA-4055
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Environment and Energy Washington, D.C. 20591		13. Type of Report and Period Covered (9) Final Report 14. Sponsoring Agency Code
15. Supplementary Notes (12) 107		

16. Abstract

The logical basis of the equations which are solved numerically in models of atmsopheric structure and composition is examined, with the conclusion that even the most advanced examples must be regarded as empirical devices to be judged by results (some of which are impressive).

The question of possible change of climate resulting from aircraft propulsion emissions into the high atmosphere is briefly reviewed. It is concluded that in the foreseen future, any impact of high altitude commercial flight on climate will be very small and not detectable against the background of natural fluctuations.

Measurements of the water vapor content of air in the upper troposphere and lower stratosphere are reviewed. They are interpreted to indicate that significant upward movement of air through a pressure level of about 100 mb, by processes of any scale, occurs only in equatorial latitudes, but they leave uncertain the mechanism of the upward transfer. Using this hypothesis, the mass balance of the nitrogen species is calculated and differences in the results of various modeling procedures are exposed.

Two phenomena peculiar to the immediate wake of the aircraft are very briefly considered - the first, the possible rapid conversion of NO to HNO_3 in the hot highly concentrated exhaust, the second, formation of condensation trails. It is suggested that in neither problem can an investigation be profitably reopened at this time.

17. Key Words Evaluation of 1-D stratospheric models, Mass balance of stratospheric species, water vapor	18. Distribution Statement This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	104	

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

FINAL REPORT

to the

FEDERAL AVIATION ADMINISTRATION
Department of Transportation

under
Contract No. DOT FA77WA-4055

The Perturbation of Some Atmospheric Mechanisms by Emissions From Aircraft

CEM Report No. 4232-667

by

G. D. Robinson
Principal Investigator

November 1979

THE CENTER FOR THE ENVIRONMENT AND MAN, INC.
275 Windsor Street Hartford, Connecticut 06120

TABLE OF CONTENTS

TABLES

FIGURES

Arrangement of the Report

The work resulted from a proposal involving three tasks, each to be based on a review of developments since publication of CIAP Monograph 3 - *"The Stratosphere Perturbed by Propulsion Effluents."* The tasks were:

- Review the several mechanisms by which aircraft exhaust emissions could affect global or local climate, with particular attention to revisions in the pattern of projected air traffic.
- Review the observations of the distribution of atmospheric trace species in the stratosphere and upper troposphere. Discuss the relevance of fine spatial detail in these measurements and the use of trace constituent concentrations in establishing parameterizations in atmospheric models.
- Review the Monograph 3 conclusion that chemistry in the immediate wake of the aircraft is of little significance in the overall stratospheric ozone reduction problem.

The report begins with a short Section on atmospheric models which reflects the personal position of the Principal Investigator (Robinson, 1978), and it is necessary to say that position apparently does not have the general support of the meteorological community (though the arguments on which it is based have not been refuted in the published literature). The main purpose of this preliminary survey is to alert the reader to the need for continued observation, both to check the conceptual validity and to monitor the predictions of even the most complex and complete models of the atmosphere. The remaining three Sections of the report address the three tasks in turn.

The Tables and diagrams are numbered separately in each Section, but because of a considerable overlap in content, a single bibliography covers the whole report.

ABSTRACT

Section 1

The logical basis of the equations which are solved numerically in models of atmospheric structure and composition is examined, with the conclusion that even the most advanced examples must be regarded as empirical devices to be judged by results (some of which are impressive). An opinion of R. C. Oliver that *"at the present state of understanding any prediction* [of climatic change involving use of the models] *should be considered primarily as a measure of risk"* is endorsed.

Section 2

The question of possible change of climate resulting from aircraft propulsion emissions into the high atmosphere is briefly reviewed in the light of:

- current projections of traffic volume and pattern,
- the most recent products of two-dimensional modeling of the problem, incorporating newly determined rate constants for key reactions, and
- recent generalized modeling of the radiative consequences of perturbations in the particle content and ozone content of the atmosphere.

It is concluded that in the foreseen future, any impact of high altitude commercial flight on climate will be very small and not detectable against the background of natural fluctuations.

Section 3

Measurements of the water vapor content of air in the upper troposphere and lower stratosphere are reviewed. They are interpreted to indicate that significant upward movement of air through a pressure level of about 100 mb, by processes of any scale, occurs only in equatorial latitudes, but they leave uncertain the mechanism of the upward transfer. This implies that contaminants emitted into the atmosphere below this level can reach the upper stratosphere only by way of the equatorial tropopause and after passage through precipitating cloud. This proviso applies to 99 percent of aircraft emission in the projected 1990 traffic pattern.

On this hypothesis, the minimum hemispheric exchange of mass through the 100 mb level is about 10^{17} kg per year. The mass balance of several minor atmospheric constituents, naturally or artificially introduced in the surface layers or in the high stratosphere, is shown to be consistent with this minimum mass exchange. Particular attention is paid to the mass balance of the nitrogen species and differences in the results of various modeling procedures are exposed. Observational programs to resolve these differences involving the nitrogen species and H_2O are suggested, with the caution that natural variability will probably mandate a protracted and expensive investigation.

Section 4

Two phenomena peculiar to the immediate wake of the aircraft are very briefly considered - the first, the possible rapid conversion of NO to HNO_3 in the hot highly concentrated exhaust, the second, formation of condensation trails. It is suggested that in neither problem can an investigation be profitably reopened at this time.

SECTION 1.0: The Basis of Modeling

1.1 The 'hierarchy' of atmospheric models

The types of model of the atmosphere which have been used in the investigation of the effects of aircraft emissions have been described in many reports generated in the CIAP and HAPP programs. The conceptual background of the 'hierarchy' of one-dimensional, two-dimensional and three-dimensional models is set out by Mahlman (1975) and Hunten (1975). An impressive illustration of the potential of three-dimensional models has been published by Levy, Mahlman and Moxim (1979) - the global distribution of N_2O produced in this effort should be compared with the observations set out by Schmeltekopf *et al.* (1977) and by Newell (1979). The paper by Schmeltekopf *et al.* contains a relevant recent application of one-dimensional modeling, and Hidalgo (1978) has reviewed recent achievements of two-dimensional modeling. The discussion which follows assumes some knowledge of the standard procedures, and analyzes them in terms of an initial arbitrary separation into those concerned with motion ('transport") and chemistry.

1.2 The nature of transport modeling

The basis for modeling atmospheric motions is the Navier-Stokes momentum equation. Robinson (1978) has contended that this equation itself is not a *"sound philosophical foundation for the belief that the state of the atmosphere can be usefully predicted by dynamical equations - even from the most precise initial specification allowed by kinetic theory."* There is, however, no other way to enter the problem; and to clarify arguments used later in this report some aspects of the standard meteorological 'primitive' dynamical equations will be set out here, by examining the local and advective acceleration terms for one component of the motion of an incompressible fluid referred to fixed rectangular axes. The terms are

$$\frac{\partial u}{\partial t} + \frac{\partial}{\partial x}uu + \frac{\partial}{\partial y}uv + \frac{\partial}{\partial z}uw \qquad (1.1)$$

the velocity components being averages over all molecules in a very small domain in space and time. In applications to the atmosphere actual initial conditions, and velocities of practical use, are averages over much larger domains. This 'useful' average is here indicated by $\bar{u}$, the 'bar operator' to be defined later. It differs from the argument of Eq. (1.1) by the fluctuation u'

$$u = \bar{u} + u' \qquad (1.2)$$

and substituting in Eq. (1.1) we have

$$\frac{\partial \bar{u}}{\partial t} + \frac{\partial u'}{\partial t} + \frac{\partial}{\partial x}\bar{u}\bar{u} + 2\frac{\partial}{\partial x}\bar{u}u' + \frac{\partial}{\partial x}u'u' + \text{other terms} \qquad (1.3)$$

The bar operator is now applied to each term of Eq. (1.3)

$$\overline{\frac{\partial \bar{u}}{\partial t}} + \overline{\frac{\partial u'}{\partial t}} + \overline{\frac{\partial}{\partial x}\bar{u}\bar{u}} + \overline{2\frac{\partial}{\partial x}\bar{u}u'} + \overline{\frac{\partial}{\partial x}u'u'} + \overline{\text{etc.}} \qquad (1.4)$$

and with axioms

$$\overline{\frac{\partial}{\partial \beta}\alpha} = \frac{\partial \bar{\alpha}}{\partial \beta}$$

$$\bar{\bar{\alpha}} = \bar{\alpha} \quad \text{i.e.,} \ \overline{\alpha - \alpha'} = \bar{\alpha} \ \text{so that} \ \overline{\alpha'} = 0 \qquad (1.5)$$

Eq. (1.4) becomes

$$\frac{\partial \bar{u}}{\partial t} + \frac{\partial}{\partial x}\bar{u}\bar{u} + \frac{\partial}{\partial x}\overline{u'u'} + \text{four other terms} \qquad (1.6)$$

Accepting for the time being the possibility of finding a 'bar operator' which satisfies the axioms, we are left with more variables than equations. If Eq. (1.6) is to be solved, the tensor $\overline{\mathbf{c}'\mathbf{c}'}$ ($\overline{u'u'}$, etc.) must be expressed in terms of the vector $\bar{\mathbf{c}}$ ($\bar{u}$, etc.) and known constants valid for all realizations of the motion. Two approaches have been used:

- *First order closure*, based philosophically, though not with physical rigour, on the mixing length approach to a theory of the turbulent motion, writing

$$\overline{\mathbf{c}'\mathbf{c}'} = K(\mathbf{r}) \frac{\partial \bar{\mathbf{c}}}{\partial \mathbf{r}}$$

where $\mathbf{r}$ is the position vector and K the 'eddy viscosity', a 3x3 array of multipliers of the elements of the gradient tensor. Note that the gradient is, of course, the gradient of the average and K depends on the scale of averaging.

- *Higher order closure*, in which an equation containing triple products $u'u'\cdot\frac{\partial u'}{\partial x}$ etc., is developed for the time derivative of the double product $\frac{\partial}{\partial t} u'u'$ etc. This development requires a further application of the axioms. The time derivative of the triple correlations may then be found in terms of quadruple correlations, and so on, the axioms being reapplied at each step. At some point the equation set is closed empirically by an algebraic relation between successive orders of correlation. These algebraic relations are based philosophically, if not always with physical rigour, on theories of turbulence, usually of homogeneous and stationary turbulence.

We now return to the question of the axioms, Eq. (1.5), and the nature of the 'bar operator'. First consider the case of a time average over Δt at a point $\mathbf{r}$

$$\bar{u}(t_o) = \frac{1}{\Delta t}\int_{t_o-\Delta t}^{t_o} u(\mathbf{r},\tau)\,d\tau$$

so

$$\bar{\bar{u}} = \frac{1}{\Delta t}\int_{t_o-\Delta t}^{t_o} \bar{u}(\mathbf{r},\tau)\,d\tau = \frac{1}{(\Delta t)^2}\int_{t_o-\Delta t}^{t_o} d\tau \int_{\tau-\Delta t}^{\tau} u(\mathbf{r},\tau')\,d\tau'$$

i.e., multiple application of this operator extends the averaged domain in time so that $\overline{\overline{u}} \neq \overline{u}$ unless $\partial\overline{u}/\partial t = 0$. Furthermore, with this operator

$$\frac{\partial}{\partial t}\overline{u} = \frac{1}{\Delta t}\frac{\partial}{\partial t}\int_{t_o-\Delta t}^{t_o} u\,d\tau = \frac{1}{\Delta t}\left[u(t) - u(t-\Delta t)\right] .$$

Application of the operator removes the time derivative of the average from the equation and successive applications of the operator, combined with the axiom, imply unchanging instantaneous velocity. Robinson (1978) elaborated this argument for various time and space averaging operations, including both the generalized weighted average and expansion in terms of the amplitudes of characteristic modes, in which case the closure device is replaced by arbitrary truncation of the mode spectrum with addition of empirical dissipative terms. It appears that the axioms, Eq. (1.5) do not hold for time and space averaging except in the trivial limit of constant uniform motion. The method thus fails to produce a prediction equation for a useful time average of a *single realization*. Equation (1.6) is a valid equation only for the instantaneous space average, over the whole domain, of the time derivative.

The basis of hydrodynamic content of the most elaborate 'primitive equation' models of atmospheric motion is, in fact, the complete form of Eq. (1.6) closed by approximation and solved by finite difference methods on a grid, or by spectral decomposition and truncation. The averages concerned are space and time averages, though the averaging time may be, and often for computational reasons must be, small. The equation cannot logically be derived from basic dynamical principles and must be regarded as an approximate empirical equation, its form suggested by analogy with the Navier-Stokes equations. However, as noted above, there is no other plausible way to enter the problem, and use of the primitive equations, or simplifications of them is standard practice in diagnostic and predictive studies of the state of the atmosphere. The purpose of the present discussion is to emphasize the need for caution in interpreting results of these studies, particularly in the predictive mode, and the continuing requirement for critical comparision with observation.

It appears to be accepted by many investigators that the higher the order of correlation at which the equation is closed, the better the approximation, in spite of the fact that repeated application has been made of axioms untenable for inhomogeneous and/or non-stationary motion. It is also intuitively reasonable, and seems to have been demonstrated numerically in trials, that the smaller the spatial domain of averaging. the better the approximation.

1.3 The nature of chemistry modeling

The basis of the modeling of chemical transformation in the atmosphere is the mass continuity equation for each modeled specie.

$$\frac{\partial \rho_i}{\partial t} = \text{div } \rho_i \mathbf{C} \quad + \text{local sources (sinks)} \tag{1.7}$$

where the sources may be, for all reactions involving specie i, of the form

$$K_{mn}\, \rho_m \rho_n \quad \text{or} \quad \int_\nu d\nu\ J\ (\nu) \rho\ \ I(\nu), \tag{1.8}$$

or may be specified sources or sinks, such as anthropogenic emissions, physical removal, etc.

In applications to the atmosphere, we can consider in practice only averages over finite domains, so that the mass continuity equation becomes -

$$\frac{\partial \overline{\rho}_i}{\partial t} + \frac{\partial \rho_i'}{\partial t} = \text{div } \left[(\overline{\rho}_i + \rho_i')(\overline{\mathbf{C}} + \mathbf{C}')\right] + \sum_{mn} K_{mn}\left(\overline{\rho}_n + \rho_n'\right)\left(\overline{\rho}_m + \rho_m'\right.$$

$$+ \overline{\text{etc.}} + \text{etc.}' + \overline{\text{boundary sources}} + (\text{boundary sources})' \tag{1.9}$$

Averaging again and applying the axioms.

$$\frac{\partial \overline{\rho}_i}{\partial t} = \mathrm{div}\left[\overline{\rho}_i \overline{\mathbf{c}} + \overline{\rho'_i \mathbf{c}'}\right] + {}_{mn} K_{mn}\left(\overline{\rho}_n \overline{\rho}_m + \overline{\rho'_n \rho'_m}\right) + \overline{\mathrm{etc.}}$$

$$+ \overline{\text{boundary sources}} \qquad (1.10)$$

where, as for the dynamical equation, Eq. (1.6), the averages are in practice space and time averages although the averaging time may be, and often for computational reasons must be, short. There is one continuity equation for each species and simultaneous solution is required. This set of equations, Eq. (1.10) has the same status as the continuity equation for averaged momentum, Eq. (1.6), in that realizable averaging procedures do not satisfy the axioms except in the trivial case of concentration and motion fields invariant in time and space. It must be regarded as an empirical approximation based on analogy with the corresponding mass continuity equation at the 'molecular scale' of averaging. Because of the terms $\mathrm{div}\, \overline{\rho'_i \mathbf{c}'}$ and $K_{mn}\, \overline{\rho'_n \rho'_m}$ the set of equations is not closed, and empirical closure procedures must be used. The usual practice in atmospheric applications has been to use a first order closure to the transport term writing it as

$$\mathrm{div}\, \overline{\rho'_i \mathbf{c}'} = \mathrm{div}\left[K(\mathbf{r}) \frac{\partial \overline{\rho}}{\partial \mathbf{r}}\right]$$

as for the momentum equation, $K(\mathbf{r})$ being a diffusivity tensor or some contraction, and a function of the scale of averaging of $\overline{\rho}$, and to neglect the concentration fluctuation correlations in the reaction terms

$$\overline{\rho'_m \rho'_n} \equiv 0$$

(In one investigation conducted in the CIAP Program (Hilst *et al.* 1973), a second order closure scheme was applied, but the transport and chemical aspects of the generation and decay of the concentration fluctuations were decoupled.)

The usual treatment of the averaged mass continuity equation thus shares with that of the momentum equation the assumption of the efficiency of the adopted closure device, but it relies also on further assumptions - that deviations of local concentrations of reacting species (including relevant photon fluxes) from the local finite difference box average are small, or uncorrelated, and that local deviations from the box average boundary and internal sources are not significant. In the case of localized anthropogenic sources of fast-reacting species, this last condition may be difficult to establish.

1.4 The comprehensive atmospheric model

The requirement for simultaneous treatment of transport and chemistry arises because the driving terms of the transport model, not yet discussed in this section, depend on temperature differences produced in part by the emission and absorption of radiation, which in turn depend on chemical composition. Furthermore, the reaction coefficients K_{mn} are, in general, temperature dependent. A complete atmospheric model must solve simultaneously the continuity equations for momentum, total energy, and mass of each chemical specie, together with the equation of state. As a particular complication, it must consider separately, as a major input to the driving terms, conversions between the three phases of H_2O. Such a model does not exist, and even if we put aside the perhaps insoluble conceptual difficulties introduced by the need for averaging, it will not exist for many years. In its absence it is not wise to assume that a model which successfully simulates one aspect of atmospheric structure, even an aspect dependent on both chemistry and transport, would satisfactorily simulate the effect of a perturbation of initial or boundary conditions, even on the same aspect of structure. It is equally unwise to assume that a model which successfully simulates one well observed aspect of atmospheric structure will satisfactorily substitute for observation of another aspect. This is not intended as a counsel of despair, merely as a reminder of the need for caution in interpretation, if such were needed in view of the recent history of investigation of the effects of aircraft propulsion effluents.

1.5 Climate models

However climate may be defined, its quantitative expression is in terms of statistics of the state of the atmosphere and a model to predict climate, diagnose possible agents of climate change, or compute the effect of anthropogenic perturbations, must handle these statistics as variables. The present writer's opinion of the current state of the subject can be summarized in three quotations, one from his own work.

In the abstract of a comprehensive and lucid review, Schneider and Dickinson (1974) write, *"Unfortunately, there is no comprehensive theory of climate to explain its variability, nor are there physical models that can adequately simulate the climatic system."* Robinson (1978) in a critique of the development, from the principles of statistical mechanics, of prediction equations for the statistics of the complex necessarily dissipative motion of real fluids writes, *"The only logically valid prediction with the types of equation now used in meteorological practice is one of no change."* Bradley (1979), concerned with, *inter alia* *"the precise solution of the essentially inviscid equations"* concludes, *"The non-equilibrium statistical mechanics which constitutes the central problem of numerical weather prediction and simulation is at present upon very shaky ground. Extensive documentation ... is necessary before any ecological policy decisions are based upon such models."*

But ecological policy decisions must be made, and no one of the authors quoted would wish them to be made without some reference to atmospheric modeling based on the best current practice. By universal agreement, the best models we have are incomplete. In this writer's opinion they will always be, in the predictive mode, logically unsound. But we have a problem which requires solution, and in the absence of sufficient observation to form a basis for empiricism or statistical estimation, the three-dimensional model is the most promising way we have to attack the problem. This writer shares with (R.C. Oliver *et al.* (1978) p. 4-7) the view that, *"at the present state of understanding any prediction* [of climate change] *should be considered primarily as a measure of risk."*

SECTION 2.0: Climatic Effects Associated with Aircraft Propulsion Effluents

2.1 Introduction

In the CIAP process and reports the convention was adopted of separate consideration of the impacts of changes in the amount of solar ultraviolet radiation with wavelength less than about 330 nm reaching the ground, and of other changes which were considered together under the term 'climate'. The separation, though convenient, is artificial; the amount and spectral distribution of solar radiation is an important aspect of climate. The distinction will not be made here, though the drastic revision, since the CIAP report, in estimates of the total O_3 column perturbation has removed any significance from this change of outlook.

This section of the report first considers some general aspects of climate and the investigation of climatic change. This is followed by a review of recent work related to the climatic effects of perturbations of stratospheric aerosol content and of changes in the ozone column. In both cases the primary perturbations considered are considerably greater than those now associated with the aircraft emissions projected over the next 20 years. Some comments are added on the problem of revision of the CIAP assessment of the climatic role of water vapour emissions.

The overall conclusion is that any climatic changes caused by aircraft propulsion effluents, in the traffic patterns visualized for the next 20 years, would not, in the present levels of climatic noise, be attributable to their cause.

2.2 Climate and the study of climate change

There have been many recent attempts to define 'climate', but from the point of view of the present report (will aircraft emissions change the climate?), the broad generalization 'statistics of weather', together with the convention that the current climatic 'normal' of any statistic is the value over a specified 30 year period in the recent past, form a sufficient definition. A climate model, to be useful in the present context, must predict the time evolution of some statistics of atmospheric structure in response to a perturbation of atmospheric composition; the first step being to predict the evolution of composition resulting from the primary perturbation. Results of two recent investigations related to the effect of aircraft emissions are discussed in Sections 2.3.1 and 2.3.3 of this report; they indicate that climatic effects of currently projected traffic will not be detectable.

The aircraft emissions problem is conveniently studied by perturbation of deterministic models of atmospheric structure. The climate system is probably the most complex interactive physical system to which the scientific method of study has been applied. In the present state of the science, the first step in an investigation of the effects of a perturbation of atmospheric composition, which can now sometimes be carried out with reasonable confidence, is to find the impact if nothing else changes. This is relatively easy with a chemically inert additive such as CO_2, but is clearly inappropriate in the case of a reactive gas such as NO. The second step is to look for obvious reactions to the primary changes. For example, one effect of CO_2 addition is to raise surface temperature, which increases H_2O content, which augments the effect of the CO_2. The primary effect is magnified and there is even a potential instability, so the third step is to look for other reactions to increased H_2O content. A comprehensive climate model would take care of all steps at the same time: the current state of modeling response to added CO_2 is that the third step has been partially considered.

A change of composition of the atmosphere changes its radiative properties and the magnitude and location of the heat sources and sinks which drive atmospheric motions and directly and indirectly determine the climate. The requirement is to identify secondary mechanisms which might increase or moderate the changes. There are three obvious potentially powerful mechanisms - adjustment of the planetary heat balance by change in amount and location of cloud, by change in the area and location of ice and snow cover, and by change in the heat content of the oceans. Manipulation of 'almost trivial' models of a system with some of the attributes of the climate system, (e.g., Fraedrich, 1978, 1979 and Sutera, 1980) indicates that the time constant of the response mechanism, relative to that of the perturbation, may have critical effect on the outcome. The mode of operation of the 'almost trivial' models is to specify 'climate' by a single parameter - temperature -, and construct a relation between this and the level of the global radiation balance. The relation has stable and unstable stationary states, and the behaviour of the system under perturbation around the stationary states is studied. The climatic effect of a composition perturbation depends, in these 'simple' parameterizations as well as in the most detailed structural models, on the associated perturbation of radiation balance, and the model response to this perturbation. A persistently applied perturbation with a potential for instability requires a rapid response mechanism if stability is to be maintained. Of the three mechanisms identified above, the first, cloud, is very rapid, of order hours. The second, ice and snow, fairly rapid, of order weeks; the third, the oceans, has a broad range of possibilities with time constants from months to perhaps 1000 years. The climatic response of the planet to materials added by man, e.g., CO_2, is not necessarily related to the rate at which the material can be removed by the natural system, which in the case of CO_2 is slow, but may be regulated by the fast response of cloud to change in the distribution of heat sources - a response which might include changes in amount, type, height of base and top, and diurnal and seasonal variability. In the most comprehensive model yet applied to the CO_2 perturbation question, neither cloud change nor ocean heat content change are adequately modeled. It may be that if these effects could be simulated, our current picture of the effect of CO_2 on climate might be greatly modified - but at present we do not even know whether any or all of the unconsidered effects are stabilizing or destabilizing. This is equally true of the addition of aircraft effluents, but the problem they pose is less forbidding than that of CO_2, since the polluting material is removed rather quickly, allowing any developing instability to be damped by regulatory action. It is shown in the following sections of this report that, in the absence of instability to very small perturbation, climatic change caused by currently contemplated levels of emissions from aircraft will be undetectable. The climatic record is sufficiently noisy to suggest that the system is, in fact, subjected naturally by internal or external mechanisms to perturbations larger than those now computed.

2.3 Recent studies of the potential climatic effect of aircraft emissions in the upper atmosphere

The problem of whether aircraft emissions in the upper atmosphere will affect the climate must be considered in two stages - firstly, in what way will the emissions change the composition of the atmosphere, and secondly, how will this change of composition affect conditions at the earth's surface? Two recent publications have made very substantial contributions to the second stage, the composition perturbations considered being, qualitatively, amongst those associated with aircraft emissions. In each case the authors stop short of predicting changes of surface climate; they concern themselves with monthly or seasonal zonal averages of components of the earth's radiation balance. The composition changes considered are in a stratospheric particle layer (Harshvardhan, 1979), and in atmospheric ozone content (Ramanathan and Dickinson, 1979). In each publication the radiative consequences of a postulated composition change are computed. The interesting circumstance is that when the computed radiative perturbations are scaled to current best estimates of the composition perturbations resulting from expected aircraft traffic patterns the result is very small, and it is suggested below that any climatic impact would be undetectable.

2.3.1 Stratospheric particle layer perturbation - sulfate particles

The first of these investigations (Harshvardhan) reexamines the radiative effect of a stratospheric particle layer, the particles being composed of 75 percent H_2SO_4 and having a specified size distribution. The radiative computations cover the full solar spectrum and the terrestrial infra-red, using tabulated optical constants for the H_2SO_4 solution. Diurnal and seasonal variations of position are considered, with alternative specifications of zonal mean cloud amount and height and of tropospheric albedo based on current climatology. Radiative terms only are modeled - the possibility of feedback of the computed perturbation on temperature and cloud distribution is ignored. The results are set out, for a particle layer with a zenith optical depth of 0.1 at 500 nm, as monthly values at 10° latitude intervals. Tables 2.1 and 2.2 summarize these results.

TABLE 2.1 (after Harshvardhan)

Perturbation of the terrestrial infra-red radiation balance by specified stratospheric H_2SO_4 particle layer with τ at 500 nm 0.1 in the zenith.

Tropical latitudes	+ 0.8 Wm^{-2}
Mid-latitude (40°) summer	+ 0.5 Wm^{-2}
Subarctic (65°) summer	+ 0.6 Wm^{-2}
Subarctic (65°) winter	+ 0.4 Wm^{-2}

(The change is a decrease in outward flux.)

TABLE 2.2 (after Harshvardhan)

Perturbation of the solar radiation balance by a specified stratospheric H_2SO_4 particle layer with τ at 500 nm 0.1 in the zenith.

Tropical latitudes			-3.8 Wm^{-2}
Mid-latitude	(40°)	summer	-4.0 Wm^{-2}
Mid-latitude	(40°)	winter	-4.5 Wm^{-2}
Subarctic	(65°)	summer	-6.0 Wm^{-2}
Subarctic	(65°)	winter	-4.0 Wm^{-2}

(The change is an increase in outward flux.)

The question of formation of sulphate aerosol from the SO_2 in aircraft emissions and the optical properties of the resulting particle layers were considered in the CIAP exercise and are reported in CIAP 3, (Robinson, Hidalgo and Greenstone, 1975) chapters 6 and 8. This work is sufficiently comprehensive to provide an estimate, valid at this date, of the perturbation of optical depth caused by specified flight patterns and fuel types. For a total injection of 10^9 kg SO_2 per year distributed in height and latitude according to CIAP 2, Table A2, (1990 traffic as estimated in 1974), and the Friend size distribution (CIAP 3, Fig. 8.8), we find a perturbation of particle load of 0.1 μgm^{-3} over a 10 km height range corresponding to an optical depth perturbation $\delta\tau$ of 4×10^{-3}, so that the expected perturbation of the radiation balance, assuming no change of cloud or temperature, would be of order 1.5×10^{-2}Wm^{-2} for the large CIAP fleet. For the current FAA high 1990 estimate of emissions, it is of order 2×10^{-3} Wm^{-2}. For a 10 Concorde fleet, (Oliver *et al.* 1978, pp. 2-23), and the transport hypothesis discussed in Section 3 of this report, the corresponding figure is 2×10^{-5} Wm^{-2}.

2.3.2 Perturbation by carbon particles

It can readily be shown that the effect of carbon soot emissions will be some orders of magnitude less than that of sulphate formed from SO_2 emissions, given the current estimate of emission index, which is 3.2×10^{-5} g carbon per g fuel. For the FAA high 1990 traffic estimate, this is an injection of 8×10^{4} kg yr^{-1} of carbon, practically all in the Northern Hemisphere. Assuming an average of one-year residence, this corresponds to a total column content above 15 km of 3×10^{-11} g cm^{-2}. Assuming a density of 2 g cm^{-3} , the number of particles of radius r is $9\times10^{-11}/8\,\pi\, r^3$ per cm^2 column and the corresponding relative geometrical cross section about $2\times10^{-11}\ r^{-1}$. For the purpose of making a maximum estimate of absorption, we regard this as an absorbing screen of thickness equal to the particle radius. We assume the very high absorption coefficient for solar radiation of 0.7 μm^{-1} (half the incident radiation absorbed by 1 μm thickness) and obtain Table 2.3.

Table 2.3 Maximum estimate of the absorbtivity of carbon particles from the 'high' 1990 emissions.

Assumed Particle Radius	Relative Geometrical Cross Section	Optical .Depth
0.01 μm	2×10^{-5}	1.4×10^{-7}
0.1 μm	2×10^{-6}	1.4×10^{-7}
1.0 μm	2×10^{-7}	1×10^{-7}

For particles of this size and absorptivity, the scattering cross section for solar radiation is not greater than the absorption, so the very roughly estimated attenuation is three orders of magnitude less than that for sulphate particles from the same aircraft emissions. It appears that the radiative and climatic consequences of carbon emissions are negligible, relative to those of the sulphate emissions, which are themselves estimated to be undetectable.

2.3.3 Ozone column perturbation

The climatic effect of perturbation in the amount and vertical distribution of ozone in the atmosphere is considered by Ramanathan and Dickinson (1979). They employ a seasonally and zonally differentiated radiative transfer model with northern hemisphere climatological temperature, H_2O, cloud and O_3, subject to various perturbations of the O_3 load. They do not treat dynamical feedback effects in detail, but estimate their importance and quantitative contribution to the problem by working with three differing assumed stratospheric temperature fields. The first assumption, made to produce a comparison standard without physical justification, is that there are no temperature changes in the stratosphere when the O_3 content is perturbed. The other two are related to the finding that in the present climate the radiative model indicates that, on the hemispheric and annual average, the stratosphere is in radiative equilibrium, i.e., the input and output of solar and terrestrial radiation combined are equal. The second case considered by the authors, termed by them 'no feedback - (NFB)' is that the O_3 perturbation does not change dynamical heating rates in the stratosphere. To maintain the overall balance the overall stratospheric radiative heating rates are not changed. With this constraint, stratospheric temperatures are changed to compensate composition changes, and the tropospheric and planetary radiation balances change. The third case, termed 'efficient feedback - (EFB)', rests on the proposition that dynamical processes react to the perturbation in a manner which maintains the stratospheric latitudinal temperature gradients in each model layer at the unperturbed values and the general level of stratospheric temperature is changed. Radiative equilibrium is maintained in the annual hemispheric average but there is no local radiative equilibrium for any averaging period. For all three cases, the primary computed parameter, on a latitudinal and seasonal basis, is the change in the net radiative input to the troposphere following a perturbation in the total amount and/or height distribution of the ozone column. The highly parameterized treatment of dynamical feedback is justified after the event, by the very small differences in radiative balance computations for the two extreme cases treated, a circumstance for which the authors find a reasonable physical explanation.

The O_3 content perturbations considered are very large in relation to current estimates of aircraft emission effects. The author's own summary of their work and conclusions cannot usefully be condensed or paraphrased and should be consulted. Table 2.4 summarizes their computations of various radiation balances following a 30 percent reduction in O_3 at all levels. The total column ozone change now associated with the high 1990 estimate of emissions is in the range ± 3 percent. However, the aspect of the Ramanathan and Dickinson work which seems most relevant to the aircraft emission problem as it is now understood, relates to changes not in the total O_3 column but in the distribution in altitude of the changes. To quote their summary:-

> *"Past studies (e.g., Ramanathan, et al., 1976) have indicated that the radiative flux changes due to ozone change depend significantly not only on the column content change but also on possible changes of the ozone profile. To further examine this possibility, we have considered the effect of vertically and latitudinally varying* O_3 *profiles, such that the net column change at any latitude and the latitudinal average of the change at any height were both zero. The assumed change was relatively small in that the maximum column change in a region of one sign was only on the order of 5% of the total* O_3 *column. Yet the flux changes in polar latitudes were comparable to, and the change in equatorial latitudes larger than, the net changes due to a 30% uniform reduction. An increase of* O_3 *in the lower stratosphere with a compensating decrease of* O_3 *at high levels (or vice versa) can apparently have an order of magnitude greater effect on the tropospheric heat balance than a monotonic ozone change of the same magnitude would have."*

TABLE 2.4 Results of the analyses of Ramanathan and Dickinson for a 30 percent reduction in O_3 amount at all levels. Power inputs in Wm^{-2}.

Latitude, Season	Column 1	2	3	4	5	6	7	8	9	10
20°, spring	−0.02	1.08	−0.25	−0.75	0.86	−0.14	0.72	0.22	−0.96	−0.74
70°, winter	−0.49	0.06	−0.33	−0.22	0.05	−0.13	−0.08	0.01	−0.42	−0.41
70°, summer	−0.16	1.37	−0.66	−0.87	1.1	−0.26	0.84	0.27	−1.27	−1.0

Notation for TABLE 2.4:

Column 1	Change in the downward flux of radiative power at the tropopause.
Column 2	Change in absorption of solar power below the tropopause.
Column 3	Change in downward emission by O_3 at the tropopause.
Column 4	The same, for CO_2 and H_2O combined. (The result of changes in stratospheric temperature.)
Column 5	Change in absorption of solar radiation at the surface.
Column 6	Change in total downward infra-red flux at the surface.
Column 7	Net change in radiation absorbed at the surface.
Column 8	Change in absorption of solar radiation in the troposphere.
Column 9	Change in absorption of infra-red flux by the atmosphere below the tropopause.
Column 10	Net change in radiation absorbed in the troposphere.

The current picuture of global ozone changes caused by expected patterns of aircraft emissions is that changes would be small, of order a few percent, and made up of an increase in the upper troposphere and lowest stratospheric levels with a decrease at higher levels. The work of Ramanathan and Dickinson shows that, for this perturbation, changes in the net radiative input to the troposphere and also the surface layers would be small. An increase of ozone in the high troposphere would tend to decrease solar and increase terrestrial radiative input to the surface layers, the latter being the larger effect, but it is not possible to predict even the sign of the radiative perturbation due to the total O_3 column change without exercising the model on a specific perturbation. In view of all uncertainties, with the final result being the small difference of larger terms, this would have little practical value until the content and pattern of emissions and the resulting composition perturbation can be definitively specified. For currently contemplated traffic patterns, it is clear that the perturbation of the troposphere/surface radiation balance would be of order $\pm$ 0.1 Wm^{-2}, with a tendency towards reduced static stability in the troposphere.

2.3.4 Perturbation of the H_2O content of the stratosphere

With an evaporative source at the earth's surface, a chemical source in the high stratosphere, and the observed vertical gradients of concentration, one-dimensional models of the entire atmospheric column inevitably accumulate H_2O at the tropopause. Two-dimensional models with empirically specified H_2O vapour transport have only recently been constructed (Widhopf and Glatt, 1979). The effect of water vapour emission was, therefore, treated in the CIAP process by a mass-balance approach rather than by detailed modeling. The natural rate of injection of H_2O from troposphere to stratosphere, and the rate of emission of H_2O into the stratosphere by projected aircraft fleets were both estimated, and the equilibrium content assumed proportional to the total injection rate. For the large 1990 fleet of stratospheric aircraft projected in 1974, the estimated increase in total stratospheric water content was about 5 percent (CIAP 3, p. 7-23). The associated perturbation of solar radiation was negligible: the rate of cooling of the stratosphere by radiation to space was found to be increased by about 5×10^{-2} °C per day. A change of one percent in stratospheric H_2O content was found to have about one-half the effect on the stratospheric cooling rate of a change of one percent in the CO_2 content, averaged over the stratospheric column. In Section 3 of this report a new hypothesis concerning exchange of H_2O

between stratosphere and troposphere is set up and its impact on modeling discussed. On this hypothesis, emission of H_2O is considered of major concern only above 16 km, so that with all but the most expansionist current traffic estimates (Oliver *et al.*, (1978), p. 2.17), H_2O originating in aircraft emissions and remaining in the stratosphere will be negligible for at least the next 20 years. A ten Concorde fleet injects about 3×10^8 kg yr^{-1} of H_2O above 16 km - only about 0.1 percent of the hypothetical natural injection. With the very large fleets of advanced SSTs considered in the CIAP process (e.g., CIAP 3, Table 6.4), the new hypothesis would approximately double the percentage perturbation estimated in that process (because of a decrease in the assumed natural annual turnover), and extrapolation of the CIAP conclusions on radiation balance in the lower stratosphere suggests that H_2O would make the largest contribution of all the aircraft effluents to perturbation of the overall radiation balance in this region of the atmosphere. This perturbation would be about half that computed to have resulted from the 10 percent increase in CO_2 content which has occurred during this century (but which has had no detected effect climatically). When the climatic impact of large fleets of aircraft - and particularly of hydrogen-fueled aircraft - flying above 16 km is reexamined, the radiative perturbation due to H_2O should be carefully considered.

The question of the effects of injection of H_2O below 16 km is raised in Section 4 of this report.

2.3.5 Changes in surface and troposphere temperature

The quoted investigations have been concerned with perturbations of the radiation balance at the surface and through the troposphere. As examples of the unperturbed values, we recall that the measured annual mean net downward radiative flux at the surface is about 45 Wm^{-2} over latitudes 50°-60°N and about 75 Wm^{-2} over 40°N to 50°N, (e.g., Robinson, 1964). The annual average radiative imbalance of the surface-troposphere system at 50°N is of order -50 Wm^{-2} (e.g., London and Sasamori, 1971). The largest perturbations discussed in connection with aircraft operations in the next 10 to 20 years are less than 0.5 percent of unperturbed value in mid-latitudes. We are concerned with the effect of this perturbation on climate. In the words of Ramanathan and Dickinson (1979), *"We do not know how much the temperature changes - or - the consequent change of vertical lapse rates* [*would be*] *and what changes this would produce --- in the climatology of atmospheric dynamic processes."* However, we note that at tropospheric temperatures the change in equivalent radiative temperature corresponding to the expected flux changes is of order 1/40°C, and that changes of order one percent in the range of diurnal variation of cloud amount or a few tens of meters in average cloud top height could balance the radiative flux changes. If a sustained average surface radiative flux change of 0.1 Wm^{-2} were partitioned between evaporation and sensible heat convection in the existing proportion, it would correspond to an average rainfall change of about 1 mm per year, 0.1 percent of the current global average. This change in turn implies a change in cloud structure which would react on the radiation balance. It will be many years before models capable of handling cloud with the degree of precision required to investigate the total climatic effect of radiative flux changes of order 0.1 Wm^{-2} are realized.

It is, however, possible to make some comparison between the radiative and climatic perturbations to be expected as a result of aircraft emissions and the predicted effects of changing CO_2 content of the atmosphere, which are at present the cause of some concern. Manabe and Wetherald (1975) applied a modified general circulation model to the CO_2 problem and computed surface temperature changes and modifications to the terms of the surface radiation balance following a doubling of the atmospheric CO_2 content. From our present standpoint, the interesting statistic of their work (combining Table 1 and Fig. 10 of their paper) is that in their model a change of

+1 Wm^{-2} in the average surface radiation balance is accompanied by an average surface temperature change of approximately +1°C. This is about four times the change in equivalent radiative temperature indicated by Stefan's law. The change of approximately 10 percent in atmospheric CO_2 content which has occurred in the present century would, on this model, correspond to a surface radiation balance perturbation of about 0.3 Wm^{-2} and a surface temperature change of 0.3°C. The magnitude of this radiation balance perturbation is about three times that which we have estimated as the result of O_3 changes for the foreseen pattern of aircraft emission. It must be emphasized that the Manabe-Wetherald model does not include cloud perturbation, although it does include evaporation and precipitation modification.

2.4 Detectability of climatic change

All series of meteorological observations exhibit fluctuations, and there is no evidence that the statistics of the fluctuations are stationary: if they are intrinsically stationary the integral time scale is longer than any observation period yet achieved. In these circumstances it is extremely difficult to relate even substantial climatic change to any anthropogenic perturbation. A combination of physical and statistical arguments is called for, but the physical system is exceedingly complex and may be intransitive* and the statistics are inadequately sampled and may be non-stationary. The most that can be hoped for is to note the coincidence of a substantial change in short term averages of a parameter with a known perturbation with which it has a physically plausible connection. There are man-made changes in local climates which have been established in this way - for example, the coincidence of a very substantial and maintained increase in winter solar irradiation in London, England with implementation of a Clean Air Act.

---

* If the statistics of solutions of the equations governing a physical system are not independent of initial conditions, the system is said to be intransitive.

The difficulties introduced by apparent non-stationarity may be illustrated by reference to the longest instrumental meteorological record - the reconstructed series of monthly average temperatures for Central England published by Manley (1953). Table 2.5 shows the standard deviation of non-overlapping averages of various durations for the period 1701-1940.

TABLE 2.5 Standard deviation of series of average temperature - Central England 1701-1940 (°C)

Duration of Average	Standard deviation of the average	
	Annual Mean	½(June & December)
80 yr	0.08	-
30 yr	0.14	0.30
10 yr	0.21	0.35
1 yr	-	1.10

Table 2.5 strongly suggests that the spectral density of variance is still increasing with decrease of frequency at the longest periods sampled. The standard deviation of the 30 year 'climatic normal' over the 240-year period is 0.14°C. Increasing the size of the sampled area might reduce this variance, but the required observations do not exist; there is reasonable coverage for perhaps three non-overlapping 30-year periods, and spatial inhomogeneity in any case compounds the sampling problem posed by the apparent non-stationarity. The inference is that climatic change of the magnitude now expected to be associated with aircraft emissions would not be detected in the sense that if it occurred it would not be convincingly attributable to its cause, certainly on a time scale less than about 100 years.

The standard deviation of annual average surface radiation balance at a single station, as currently measured, is of order 10 percent (5 to 10 Wm^{-2}) in temperate and tropical latitudes. Direct detection of time-averaged surface radiation balance changes of order 0.1 Wm^{-2} is far beyond current instrumental capability and likely to remain so, except at inordinate cost.

SECTION 3.0: Some Aspects of the Transport of Trace Gases in the Atmosphere

3.1 Arrangement of this section

The Section begins with two short subsections commenting on the uses of observations of trace gas concentration and on its essentially fluctuating magnitude. Two sections (3.4 and 3.5) follow in which observations of the distribution of concentration of firstly, H_2O, and secondly, various other trace constituents, are interpreted in terms of a hypothesis concerning mass exchange between the troposphere and the stratosphere which considerably restricts the possible modes of transport between the sources and sinks of trace gases. A paper based on this work has been accepted for publication by the Royal Meteorological Society.

Subsections 3.6 and 3.7 discuss the results of selected models of the mass balance and concentration of the nitrogen species of interest in the aircraft pollution problem, comparing them with observation and indications of the transport hypothesis. In subsection 3.8 some suggestions concerning future observations of trace gas concentration are made.

3.2 Relevance of trace gas concentration observations to the FAA problem

In the broadest terms the problem under study is, "what effect will propulsion effluents from aircraft operating at high altitude have on life on the planet?" The initial step is to answer the question, "what effect will these effluents have on the composition and structure of the atmosphere?" Quantitative study involves the use of mathematical models of the atmosphere which include chemical, thermodynamical and dynamic processes. What part do trace gas measurements play in the construction, operation, and validation of these models? Some aspects are:

(a) *Selection of relevant chemistry*

For example, H_2O, CH_4, CO and N_2O were known to be present, and some aspects of their distribution were known, before intensive study of the aircraft emissions problem began. On the other hand, there were no reliable observations of NO and ClO before their potential importance was theoretically demonstrated and it became necessary to confirm their presence.

(b) *Qualitative tracing of atmospheric motion*

An example is Brewer's explanation of the humidity structure in the lower stratosphere, further developed in Section 3.4 of this report. For some purposes quantitative development of the qualitative indications (which may be difficult) is unimportant - for example, some types of motion simply cannot be consistently simulated by some types of model. If that type of motion is found to be important in any context, the corresponding model will not be consistently reliable in that context.

(c) *As quantitative input to the parameterization of transport terms in any model*

The obvious example is the use of observations of N_2O and CH_4 concentration to determine the eddy diffusivities in the one-dimensional models used in the first assessments of the impact of aircraft emissions.

(d) *To provide initial and boundary values for concentration and flux terms in the operation of models.*

(e) *To provide reference standards for the validation of models.*

3.3 The general nature of trace gas concentrations

If a trace gas is of interest in stratospheric chemistry, it will have a position- and time-dependent concentration. If it has more than an ephemeral life, atmospheric motion, which may have magnitudes of order 100 ms^{-1} in the middle and high stratosphere, will ensure that point values of concentration will fluctuate in time and that the structure of instantaneous distributions may differ considerably from time-average distributions. The variance of concentration will depend on position and on the large scale sources and sinks of the species concerned. The only physical justification of eddy diffusivity parameterizations of atmospheric transport, the mixing length concept, calls for time averaging of concentration fields: eddy diffusivities derived from one or a few sets of observations may, therefore, be grossly misleading. Observations of concentration variance are potentially as important as averages - the only physically sound way of estimating transport of a trace substance across a surface is to integrate over area and time the product of the local instantaneous values of concentration and air velocity normal to the surface. Full understanding of the life-cycle of a chemically active trace constituent of the atmosphere may, therefore, call for a very large number of observations over an extended period. We are in a position to estimate the magnitude of the task in the case of only one chemically active trace gas - ozone. This has been observed by a variety of techniques for a period of about 50 years on a global basis (including 10 years of satellite surveillance). We still do not understand some aspects of its incidence - for example, is there a secular variation of total atmospheric ozone content? What would we know about the ozone problem if we had only as many observations of O_3 as we have of N_2O, CH_4, or even H_2O? It follows that extreme caution should be exercised in arguing from the few observations we have, whether in constructing or in validating atmospheric models. When such an argument is the only one open, its indication should indeed be "considered primarily as a measure of risk". It is equally difficult to plan an observing program specifically to confirm a theoretical finding or validate a model calculation, unless very large resources can be made available over a period of years. Some examples of these difficulties are exposed in the following sections of this report.

3.4 Exchange of H_2O between troposphere and stratosphere - a transport hypothesis.

In this section a hypothesis concerning the transfer of air between troposphere and stratosphere is set up and examined. It is qualitatively, that proposed by Brewer (1949), and like his is based on observations of H_2O concentration, but its quantitative aspects are differently derived. Since we are to treat transport across it, it is useful first to recall the definition of the tropopause - "*The first tropopause (i.e., the conventional tropopause) is defined as the lowest level at which the lapse rate decreases to 2°C* km^{-1} *or less, and the average lapse rate from this level to any level within the next higher 2 km does not exceed 2°C* km^{-1}......" The local position of this conventionally specified feature of a temperature-height plot can change, without change of the total mass of the stratosphere, by radiative adjustment and by movement of air. The hypothesis to be examined is concerned with the scale and nature of the air movements responsible for the major changes in the zonally averaged tropopause position which do imply a change of total stratospheric mass.

3.4.1 Outline of the Argument

In this section certain observed facts and those broad features of their interpretation which lead to the mass transfer hypothesis will be set out, without regard to some niceties and difficulties which will appear later.

(a) *Water content of stratospheric air*

The mass mixing ratio (mmr) of H_2O in most of the air in the stratosphere is 2 to $3x10^{-6}$.

(b) *Sources of sinks of atmospheric* H_2O

There is no significant chemical sink of H_2O in the atmosphere. There is almost certainly a chemical source of significant magnitude in the high stratosphere. The major source is evaporation at the earth's surface; the only identified sink is the process of cooling, condensation and precipitation. Table 3.1 shows the state of air with mmr 2×10^{-6} and 3×10^{-6} in equilibrium with ice. In the atmosphere these conditions occur frequently in the antarctic winter above about 100 mb, fairly frequently at the equatorial tropopause, and very occasionally in the arctic winter above 100 mb. The bulk of stratospheric air must have passed through one of these regions. For convenience, we will refer to this process as the "freeze-dry process".

TABLE 3.1 Approximate pressure (mb) for saturation over a plane surface of ice according to the Smithsonian Meteorological Tables. (Goff-Gratch formula)

	Temperature K				
mmr	188	190	192	194	196
2×10^{-6}	70	98	138	192	265
3×10^{-6}	46	66	92	128	177

(c) *Variation of the mass of the stratosphere*

Figure 3.1, due to E. M. Danielsen (Reiter *et al.* [1975] p.6-21) illustrates the averaged height of the tropopause in the Northern Hemisphere on one line of longitude (78°W) in February and July of one year (1958). That it may not be appropriate to other longitudes and dates may be seen from Fig. 3.2, in which each dot represents the position of the tropopause over southern England (~1°W, 50°N) on days between 1950 and 1956 when aircraft of the Meteorological Research Flight made measurements of H_2O concentration at high levels. There is little sign of regular annual variation of mean height and the averages for February and July differ considerably from those for 50°N on Danielsen's diagram. Faith in the significance of Fig. 3.1 is, however, at least partially restored by Fig. 3.3 in which the lines ABC′ and D′EFG represent, respectively, the "polar" and "equatorial" tropopauses, and the vertical lines DB and EC the mean winter and summer positions of the vertical axis of the maximum in the zonally averaged winds (the 'subtropical jet'). The spread in latitude of these mean positions covers the various estimates reported by Lorenz (1967). The implication of Fig. 3.3 is that about 20 percent of the mass of the northern hemisphere's stratosphere is exchanged annually. The exchange is with the troposphere. A direct indication of this is the annual variation in the deposition at the earth's surface of stratospheric radioactive contaminants and its concentration in mid-latitudes, and observed winds and momentum balance considerations show that the rapid exchange is not substantially with the temperate and polar southern hemisphere stratosphere. The antarctic winter stratosphere is not the source of the air which replenishes the lower northern hemisphere stratosphere between July and February each year. The only remaining potential "freeze-dry" source is at the equatorial tropopause.

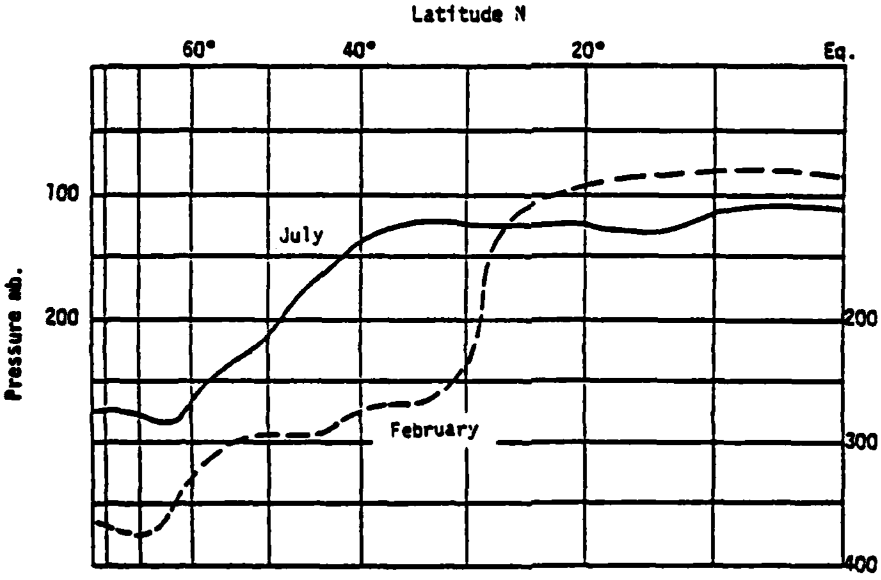


Fig. 3.1 Average tropopause position at 78°W in 1958. (Danielsen)

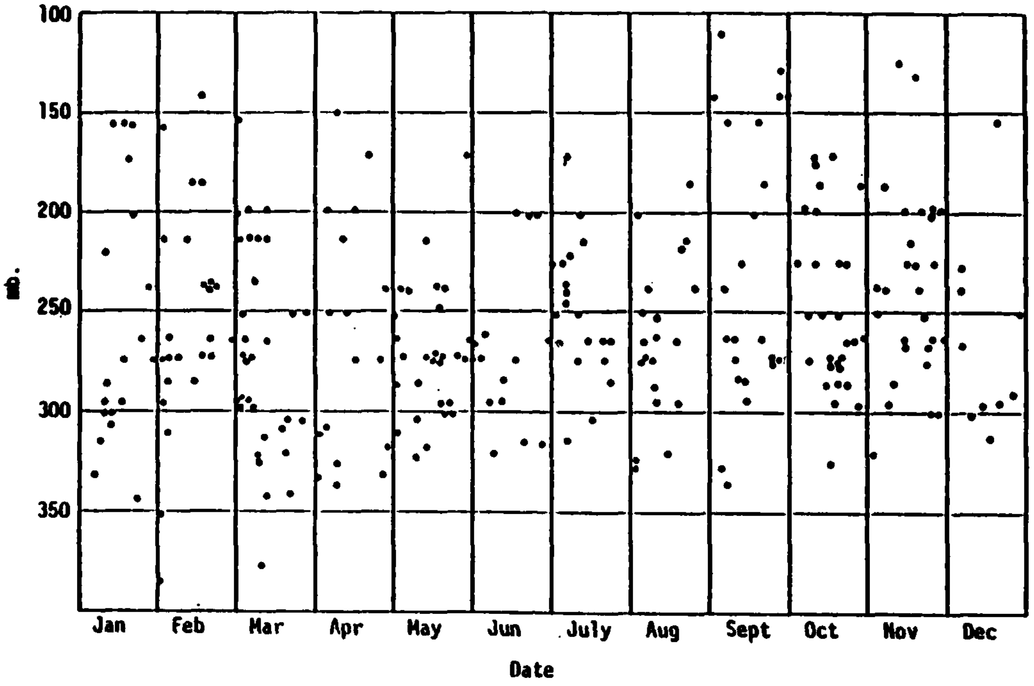


Fig. 3.2 Reported position of the conventional tropopause over Southern England on days when high level humidity was measured, 1950-1955.

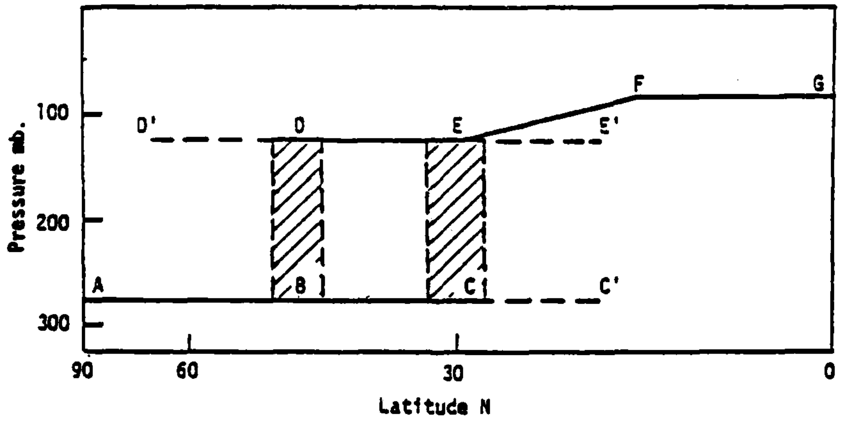


Fig. 3.3 Illustrating the mass transfer hypothesis.

(d) *Air motion at the equatorial tropopause*

There is evidence of a net rising motion of air at the equatorial tropopause. It is discussed at some length, in the context of the water budget of the stratosphere, in Reiter *et al.* (1975) Section 3.3 and Robinson *et al.* (1975) Chapter 7. Estimates of its magnitude have been made by four methods - convergence of the observed horizontal wind fields, contribution of the "advection of potential energy" to the global energy budget, the operation of comprehensive general circulation models, and balancing by adiabatic cooling of the radiative heating of the atmosphere near the tropopause. Each method of estimation has uncertainties of at least a factor of two - the fourth particularly because of the difficulty of assessing the role of high cloud. Of the four arguments, only the last implies a slow steady toroidal circulation. The others imply only poleward mass motion in the upper atmosphere, which could arise from sporadic local injection of air, for example in convective cloud, not totally compensated by local downdraft, as well as from steady slow circulation.

(e) *Fluctuations of the stratospheric H_2O mixing ratio*

The observations of stratospheric mixing ratio which will be considered are effectively instantaneous point values, not space or time averages smoothing the changes in a possibly fluctuating quantity. The range of observed values is very limited and establishes that if there is any significant entry of air with substantially higher mmr than 3×10^{-6}, it must be compensated by entry of a larger quantity of air with lower mmr than 3×10^{-6}. There is no identified source of such air but if there were, very rapid intimate mixing of the two air masses would be required to explain the observations.

(f) *Air motion at the tropopause gap*

In Fig. 3.3 the zones DB and EC represent, respectively, the zonal mean winter and summer positions of the "tropopause gap". Figure 3.4 represents an instantaneous section along one longitude. It is known that there is exchange of tropospheric and stratospheric air through this gap, as indicated by the arrows in Fig. 3.4, and there is convincing evidence, of the type first presented by Danielsen (1959), of descent of air of recent stratospheric origin to levels below the extension CC´ of the polar tropopause - the region K of Fig. 3.4. Water content measurements, however, show no evidence of corresponding penetration of air of recent tropospheric origin to levels above the extension DD´ of the tropical tropopause, i.e., into the region L of Fig. 3.4. The H_2O mmr is a sensitive test: a representative state of the air in the gap region is temperature 210K, pressure 200 mb, at which the mmr for saturation with respect to ice is about 35×10^{-6}.

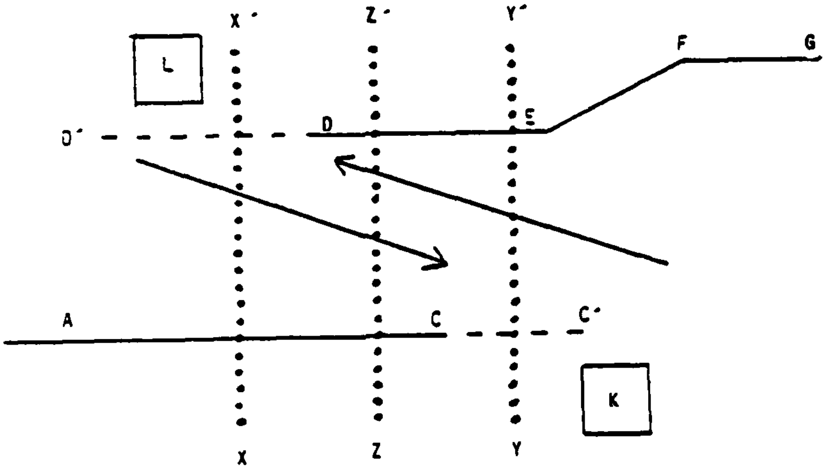


Fig. 3.4 Schematic diagram of the 'tropopause gap'

3.4.2 The mass transfer hypothesis

The mass exchange hypothesis to be examined is that air does not cross from below the level marking the position assumed by the equatorial tropopause at any time of year, i.e., the line D´DEFG of Fig. 3.3, except in the equatorial sector FG; and that the minimum annual hemispheric mass exchange is the content of the "box" DBCE of Fig. 3.3 - the mass difference between the winter and summer hemispheric stratospheres. This mass is approximately 10^{17} kg of air. It is effectively the same as the mass difference between the July and February stratospheres of Danielsen's diagram, Fig. 3.1.

In the absence of observations, the hypothesis does not exclude direct upward transport from the troposphere to the high stratosphere poleward of the point D, the polar limit of transient incursions of the tropical tropopause. In the North Atlantic sector, and probably in the Alaskan sector, this point is poleward of 70° so that the area available for such upward transport is small.

Exchange through the tropopause gap below the line D´E as illustrated in Fig. 3.4 is not limited in the hypothesis but is a transient phenomenon, 10^{17} kg of air being the minimum net annual outflow. Similarly, transient (quasi-vertical) exchange across the tropical section FG is not excluded, 10^{17} kg is the minimum net annual upward flow. Spread uniformly over a 15°latitude band, this implies a mean vertical velocity at the tropopause of about 2×10^{-4} m $\sec^{-1}$.

3.4.3 A review of the observations of water content

Harries (1976) described the measurements of stratospheric H_2O content available prior to 1976, but he did not treat in detail the region close to the tropopause which is the main concern of this paper. There is considerable variability in the measurements reviewed by Harries and the extent to which this reflects measurement error is not resolved. The difficulty of stratospheric water measurements must be kept in mind: the possibility of spuriously high values due to contamination of equipment is always present with every type of measurement. There has been a tendency by experimenters to reject very high values, with less emphasis on the possibility of minor contamination in all measurements, resulting in systematic overestimation. On the other hand, systematic errors in the measurement of deposit temperature in frost-point hygrometers are not easy to eliminate and these could result in underestimates of concentration (Oliver and Cluley, 1978). Explanation of the stratospheric H_2O distribution is further complicated by a possible increase of perhaps 50 percent in the concentrations measured in the lower stratosphere over the 30-year period in which observations have been made - evidence for which is presented by Harries (1976), Mastenbrook (1971), and Cluley and Oliver (1978). Mastenbrook (1974) suggests that the rising trend ceased around 1970 and the few more recent measurements of Kley *et al.* (1979) appear to confirm the earlier low values. The present investigation centers on the fact that above the upper 'line' of Fig. 3.3, there are very few measurements of H_2O concentration greater than a value which we set nominally at $3x10^{-6}$ - perhaps $2-3x10^{-6}$ in the 1950s and $3-4x10^{-6}$ in the 1970s - and does not further consider possible secular change.

The discussion is mainly concerned with four types of measurement. Those by the MRF were made with a manual frost-point hygrometer operated on an aircraft in level flight. A single measurement occupied up to five minutes, during which the aircraft covered at most 50 km. Those by Mastenbrook were made with a balloon-borne automatic frost-point hygrometer. The time constant of the instrument is not specifically stated, but published mixing ratios are the average of six determinations during which the balloon ascended about 1 km, centered on the datum point. Those by Kuhn were deduced from aircraft measurements of the downward directed flux of thermal radiation in a band dominated by H_2O emissions. Kuhn's reduction technique involves certain assumptions concerning the distribution of H_2O above the point of measurement, but is not sensitive to reasonable variation of these assumptions. His measurements are presented effectively as point values, not differenced overburden. The measurements of Kley *et al.* are of the OH fluorescence produced when H_2O is photolyzed by Lyman-α irradiation. A very small volume is irradiated and the signal integrated over 1 sec or about 30 m height. As stated in Section 3.4.1e, we consider all these measurements to be effectively instantaneous point values.

The evidence will be presented in two ways - frequency diagrams and tables of mixing ratio at different heights, and details of particularly interesting individual profiles. The frequency diagram display was adopted by Mastenbrook (1968). Observations over extended periods are available in only three locations. Over southern England (~50°N 0.5°W), they were made by the High Altitude Flight (1943-1946) and Meteorological Research Flight (MRF) (1946-1955 and 1972-1976) of the Royal Air Force. These observations are reported by Bannon, Frith and Shellard (1952), Tucker (1957), Murgatroyd, Goldsmith and Hollings (1955), Helliwell, MacKenzie and Kerley (1957), and Cluley and Oliver (1978). In the neighborhood of Washington. D.C. (~40°N 75°W), the measurements, by balloon borne equipment, are due to Mastenbrook (1968, 1971, 1974) who reported results covering the period 1964-1973. Mastenbrook (1968) also reported measuremens over Trinidad, W.I. (~10°N 60°W) during 1964-1965. Measurements elsewhere have been made over short periods on an expeditionary basis. Mastenbrook (1968) made three balloon ascents over Thule, Greenland (77°N 69°W) in summer. The MRF operated over East Africa (10°S-10°N ~37°E) and Aden (13°N 45°E) (Kerley, 1961), over and to the south of Tripoli (~32°N 15°E) (Helliwell and Mackenzie, 1957), and on traverse ranging from about 40°N to 70°N near the prime meridian (Helliwell, (1960), Roach (1962), Cluley and Oliver (1979)). Aircraft performance limited the RAF ascents to about 190 mb before 1954 and to about 125 mb at later dates. In the summer of 1977, an expedition mounted by the Ames Research Center of NASA explored phenomena in the intertropical convergence (ITCZ) near Panama (10°N 80°W). P. Kuhn, using the radiometric method described by Kuhn, Magaziner and Stearns (1976) made water content measurements to the

45 mb level. Finally, Kley *et al.* (1979) perfected the Lyman-α fluorescence technique and made three balloon-borne soundings at Laramie, WY (45°N 105°W) and one at Quixeramobim, Brazil (5°S 39°W).

(a) *Extratropical measurements of water content*

Figures 3.5 to 3.7 are frequency diagrams in the form introduced by Mastenbrook for the three extratropical localities where sufficient observations are available. Mastenbrook's (1974) diagram for Washington, D.C. is reproduced for ease of comparison. In each diagram a vertical line separates observations with mixing ratios less than and greater than $3x10^{-6}$. If this limiting value is increased to $4x10^{-6}$ to cover the indicated general secular changes, the data suggest that the upper 'line' of Fig. 3.1 or Fig. 3.3 is at about 130 mb over southern England, and about 110 mb over Washington, D.C. The MRF observations in level flight at 140 mb over the latitude range 40°N to 70°N are summarized in Table 3.2. They are inconclusive because of the height limitation; the high humidities reported between 57°N and 62°N by Roach (1962) at 140 mb and by Cluley and Oliver (1979) at 147 mb are interesting but not obviously inconsistent with the mass transfer typothesis, since they lie below the extension DD' of the upper 'line' in Fig. 3.3. There are other indications scattered amongst unpublished reports, as well as in the open literature, not individually conclusive, which suggest that air of recent tropospheric origin may occasionally be found at levels up to 100 mb at latitudes about 60°N in summer and that the situation here deserves further study.

The three Laramie ascents of Kley *et al.* are summarized, over the range of our interest, in Table 3.3. They are consistent with the Washington observations at the same latitude, and are particularly valuable in confirming closely the indications of the two types of frost-point hygrometer. Mastenbrook's Greenland observations are summarized in Table 3.4. They are consistent with the mass transfer hypothesis, and in particular indicate no quasi-vertical large-scale transport of tropospheric air at this polar location in summer.

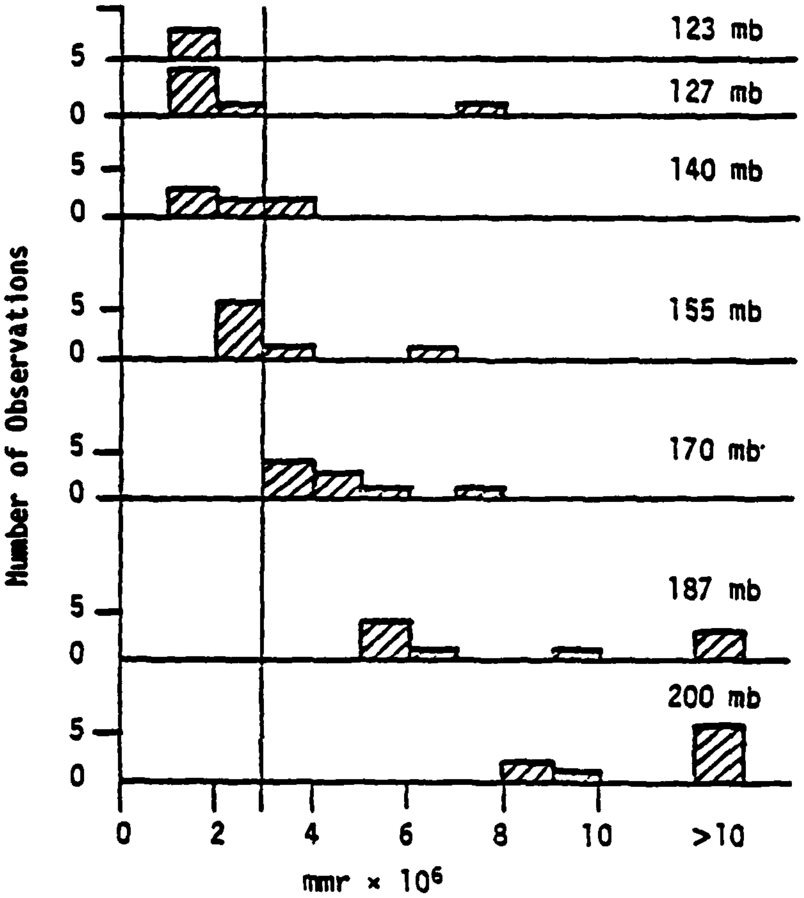


Fig. 3.5 Frequency diagram, mass mixing ratio of H_2O, Tripoli, May 1956

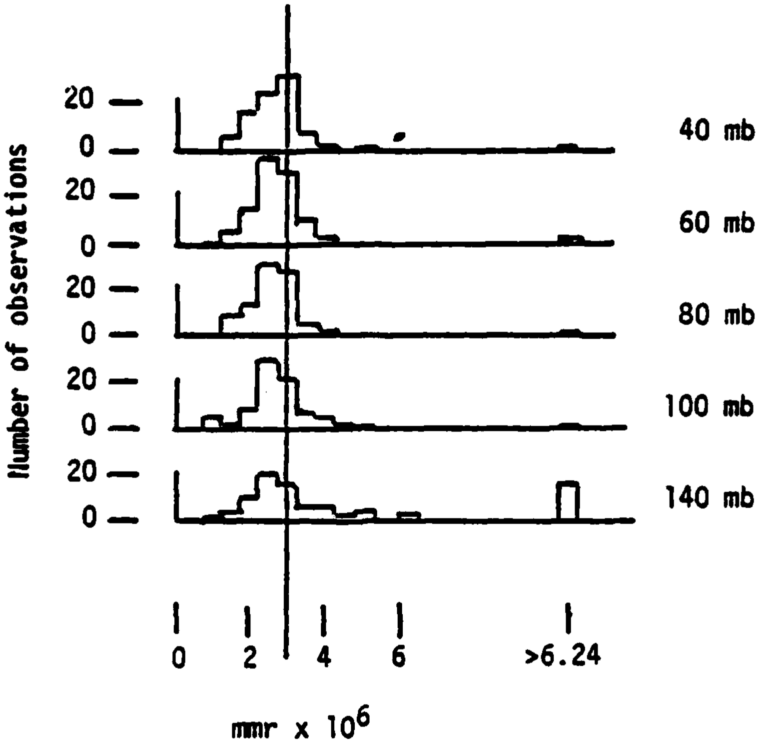


Fig. 3.6 Frequency diagram, mass mixing ratio of H_2O
Washington, D.C., 1964-1973
(Mastenbrook, 1974)

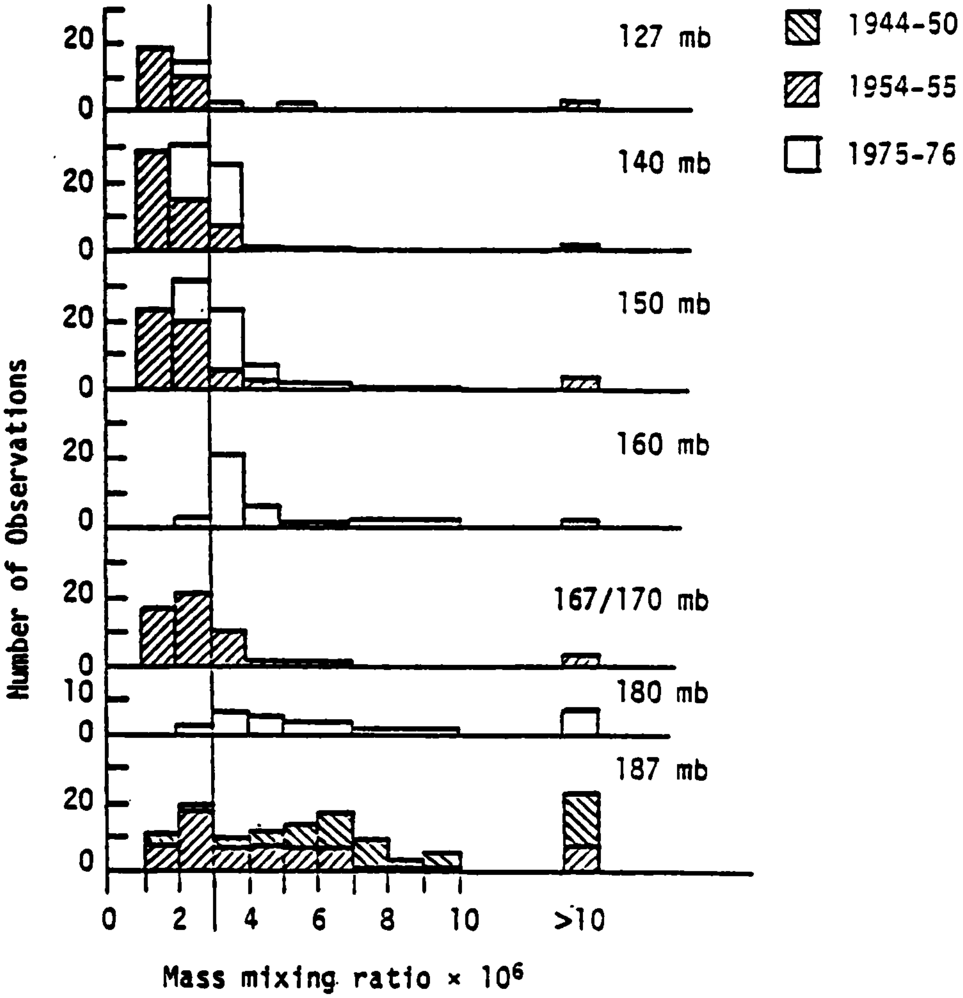


Fig. 3.7 Frequency diagram, mass mixing ratio of H_2O Southern England, 1944-1976

TABLE 3.2 Number of observations in various ranges of the mass mixing ratio of H_2O in the upper atmosphere, 42°N-67°N 5°E-5°W.

Latitude	Pressure		mmr x 10^6						
°N	Level mb	Period	<2	2-2.9	3-3.9	4-4.9	5-6.9	7-9.9	10
42	140	1956/57	2	3	2	-	-	-	-
	187		-	1	1	-	-	1	-
	205/255		-	-	1	-	-	1	-
47	140	1956/57	2	2	1	-	-	1	-
	187		1	1	-	1	-	-	-
	205/255		-	-	-	1	-	1	-
52	140	1956/57	1	4	-	-	-	-	-
57	140	1956/57	1	4	1	-	-	-	-
	187		-	2	1	-	-	-	-
60	140	1962	2	4	-	-	1	1	-
	170/187		1	1	-	1	-	2	-
	205/255		-	1	4	-	-	-	2
61	147	1977	-	-	1	1	1	-	1
	160		-	-	-	2	1	-	-
	180		-	-	-	-	2	2	-
62	140	1956/57	3	3	-	-	-	-	-
	187		-	2	1	-	-	-	-
	205/255		-	1	1	-	-	-	-
63	160	1977	-	-	-	-	-	-	1
	180		-	-	-	-	-	1	-
65	147	1977	-	-	-	-	-	1	-
	160		-	-	-	-	-	1	-
	180		-	-	-	-	-	1	-
67	140	1956/57	4	2	-	-	-	-	-
	187		-	3	-	-	-	-	-
	205/255		-	2	-	-	-	-	-
	147	1977	-	-	2	-	-	-	1
	160		-	-	-	2	-	-	1
	180		-	-	-	-	1	1	1

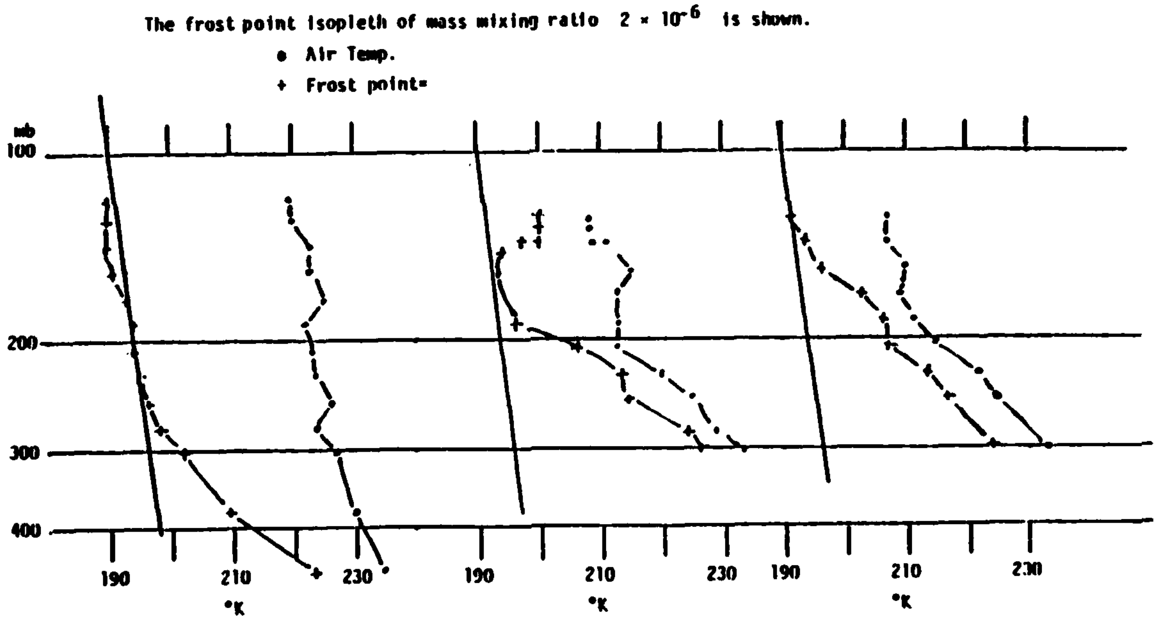
TABLE 3.3 Measured mass mixing ratio of H_2O at Laramie, WY 42°N-105°W in July and September 1978 and January 1979 (Kley *et al.* 1979)

Pressure mb	mmr x 10^6		
200	12	7.0	2.2
140	3.8	4.2	2.2
120	3.5	6.0	1.9
100	3.5	3.5	2.3
80	2.4	2.3	2.3
60	2.5	2.6	2.6
40	3.0	3.2	2.4

TABLE 3.4 Measured mass mixing ratio of H_2O at Thule, Greenland 77°N-69°W in 1965 (Mastenbrook, 1968)

Pressure mb	mmr x 10^6		
200	4.0	3.5	2.8
180	3.3	2.9	2.5
140	2.7	-	1.7
120	2.7	-	1.6
100	2.9	-	1.5
80	2.8	-	1.7
60	3.0	-	2.0
40	2.5	-	1.5

Figure 3.8 contains details of three aircraft soundings chosen to illustrate the situation idealized in Fig. 3.4; one Southern England, 10 February 1955, presumably in position XX´ of Fig. 3.4, one Southern England, 29 September 1955, presumably in position YY´, and the third a composite of climb and N-S traverse, over and to the south of Tripoli, 27 May 1956, known to be close to the jet axis in position ZZ´, but not reaching the upper tropopause. A possible explanation of this ascent is that it shows air of recent tropospheric origin lying above air of recent stratospheric origin near the jet core.



a. 10 Feb 1955
Southern England
XX´ of Fig. 3.4

b. 27 May 1956
South of Tripoli
ZZ´ of Fig. 3.4

c. 29 Sept 1955
Southern England
YY´ of Fig. 3.4

Fig. 3.8 Atmospheric temperature and humidity soundings related to the tropopause gap.

(b) *Tropical water content measurements*

Figures 3.9, 3.10 and 3.11 are, respectively, frequency diagrams of H_2O content observed at Nairobi/Aden, Panama and Trinidad, Fig. 3.11 being reproduced for ease of reference from Mastenbrook (1968). In each diagram the frequencies of corresponding ranges of saturation mmr at the lowest temperature recorded on the balloon ascent (or in the case of aircraft observations, the nearest radiosonde ascent) are indicated. The MRF ascents summarized in Fig. 3.9 were not made in the vicinity of active convective cloud. The aircraft did not reach the tropopause but the mmr at the highest point reached was never greater than that corresponding to saturation at the tropopause. The Panama and Trinidad diagrams are remarkably similar, in view of the fact that those at Trinidad cover all seasons of the year. They show that, as in the Nairobi ascents, the mmr over a considerable height range is often less than that corresponding to saturation at the lowest temperature on the ascent. Some of the implications of this are better exposed by study of individual ascents; this can be made with more confidence after noting the similarity of results from the frost-point hygrometer and from Kuhn's radiometric technique.

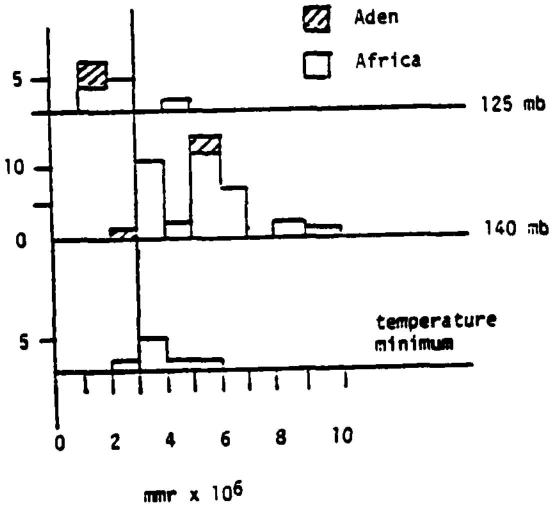


Fig. 3.9 Frequency diagram, mass mixing ratio of H_2O and saturation mmr at the temperature minimum, Africa 10°N-10°S and Aden June 1958.

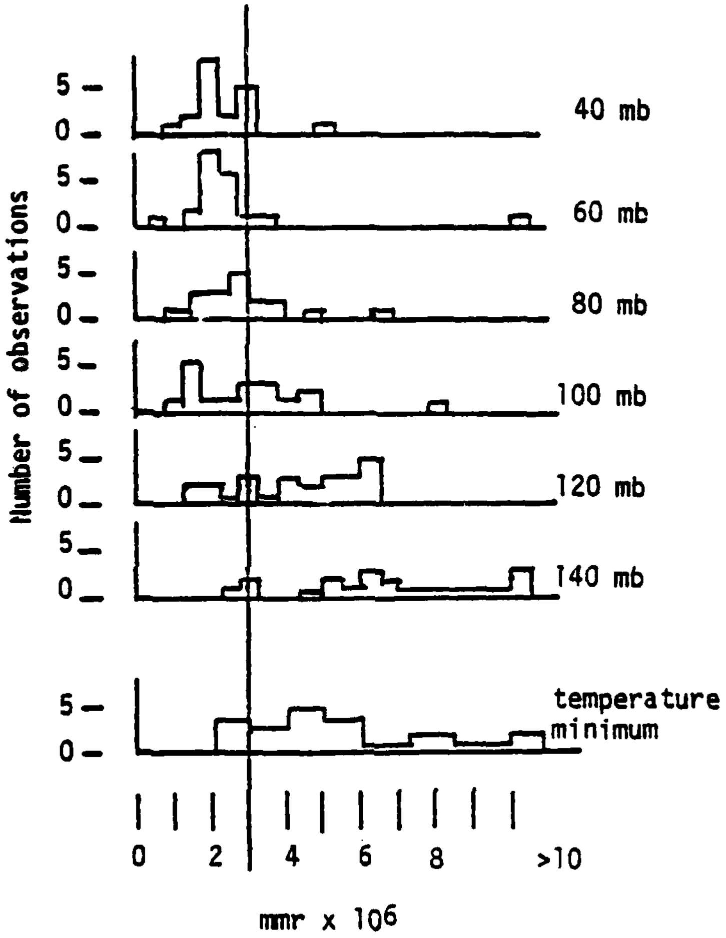


Fig. 3.10 Frequency diagram, mass mixing ratio of H_2O and saturation mmr at the temperature minimum. Trinidad, W.I. 1964-1965 (Mastenbrook)

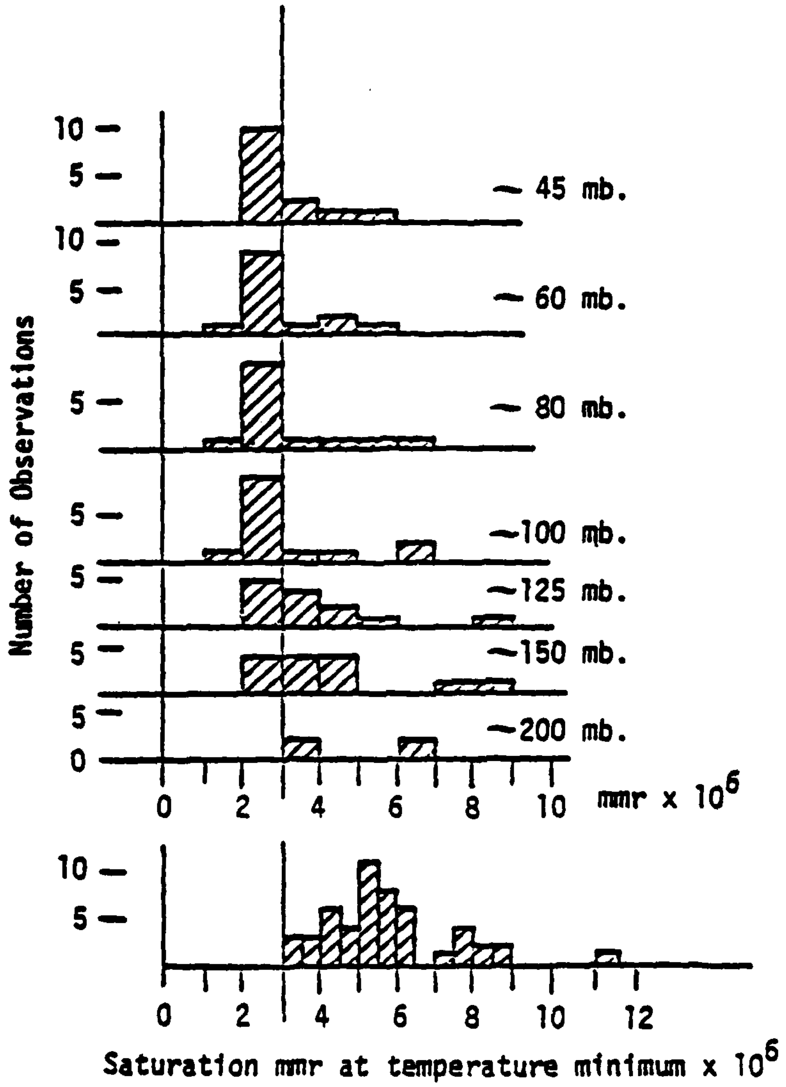


Fig. 3.11 Frequency diagram, mass mixing ratio of H_2O and saturation mmr at the temperature minimum. Panama 17-31 July 1977. (Kuhn)

In his preliminary analysis of the 1977 Panama measurements, Kuhn divided the ascents into 'wet' and 'dry' occasions, and Figs. 3.12 and 3.13 illustrate one of each type. Details from two daytime radiosonde ascents are plotted on each of these diagrams. Fig. 3.12 illustrates a 'dry' day. The mmr falls slowly from about $4x10^{-6}$ at 200 mb, well below the tropopause, to $2.5x10^{-6}$ at 50 mb. The saturation mmr corresponding to the conventional tropopause temperature is $9x10^{-6}$ and that to the temperature minimum about $6x10^{-6}$ on one radiosonde ascent and $7.5x10^{-6}$ on the other. This is the type of behaviour indicated as common by the frequency diagrams. The annotations on Fig. 3.12 refer to the pilot's report and to the occurrence of rapid changes during horizontal flight in the recorded O_3 concentration. Fig. 3.13 illustrates a 'wet' day. The aircraft did not enter cloud, but between 140 and 100 mb the mmr corresponded to saturation at ambient temperature. The mmr remained constant at about this value - 5 to $6x10^{-6}$ - up to the highest level, about 45 mb. On this day the flight was conducted in the vicinity of large convective cloud, and the pilot reported Cb tops visible at an estimated pressure level about 70 mb, with a conventional tropopause about 140 mb. The reported cloud top level was close to that indicated for 'adiabatic overshoot' by the radiosonde ascents (see e.g., Roach, 1967).

Other examples of the humidity structure at the tropical tropopause are shown in Fig. 3.14. The Quixeramobim ascent using the Lyman-α technique has saturation at a tropopause with mmr $3x10^{-6}$, but within the next 30 mb the mmr falls to less than $2x10^{-6}$ and remains at that level over a considerable height range. The Nairobi ascent is saturated in cirrus at 140 mb, but the mmr has fallen to about $2x10^{-6}$ at 125 mb, well below a tropopause with saturation mmr $4x10^{-6}$. The Aden ascent of 25 June 1958 is saturated in cirrus at 200 mb, but again the mmr has fallen to $2x10^{-6}$ at 125 mb. The radiosonde apparently did not reach the tropopause on this day. At Aden on 20 June 1958, the aircraft did not reach a layer of thin cirrus, reported above 125 mb at which level the mmr was $3x10^{-6}$. The saturation mmr at the tropopause was $2x10^{-6}$.

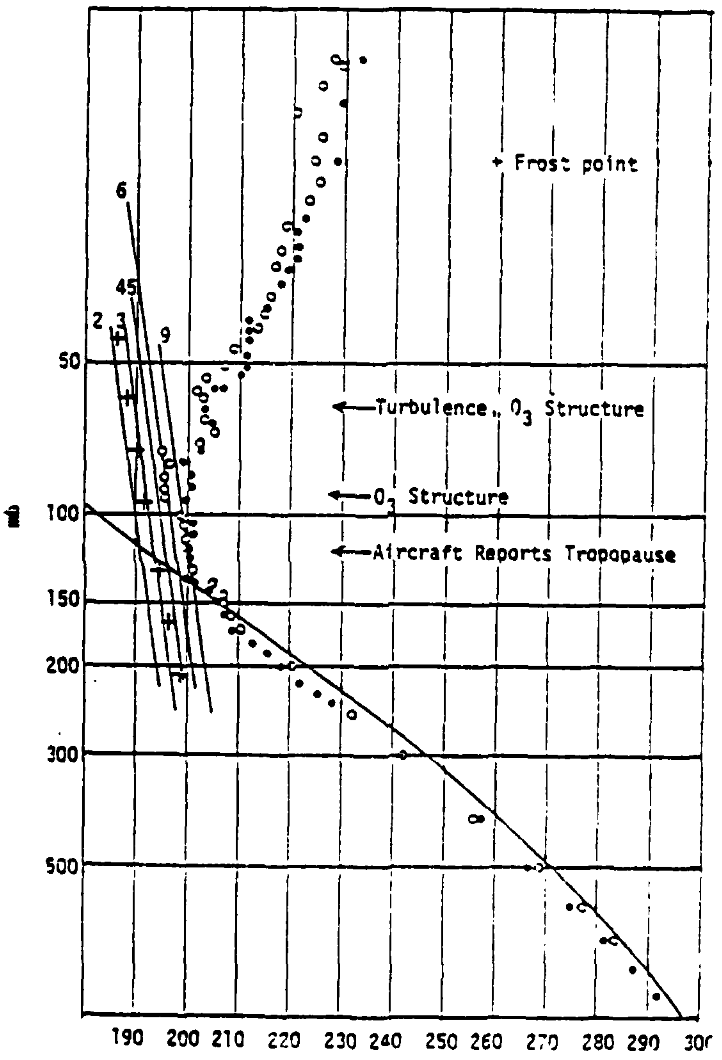


Fig. 3.12 Radiosonde temperatures and aircraft humidity sounding.
Panama 27 July 1977

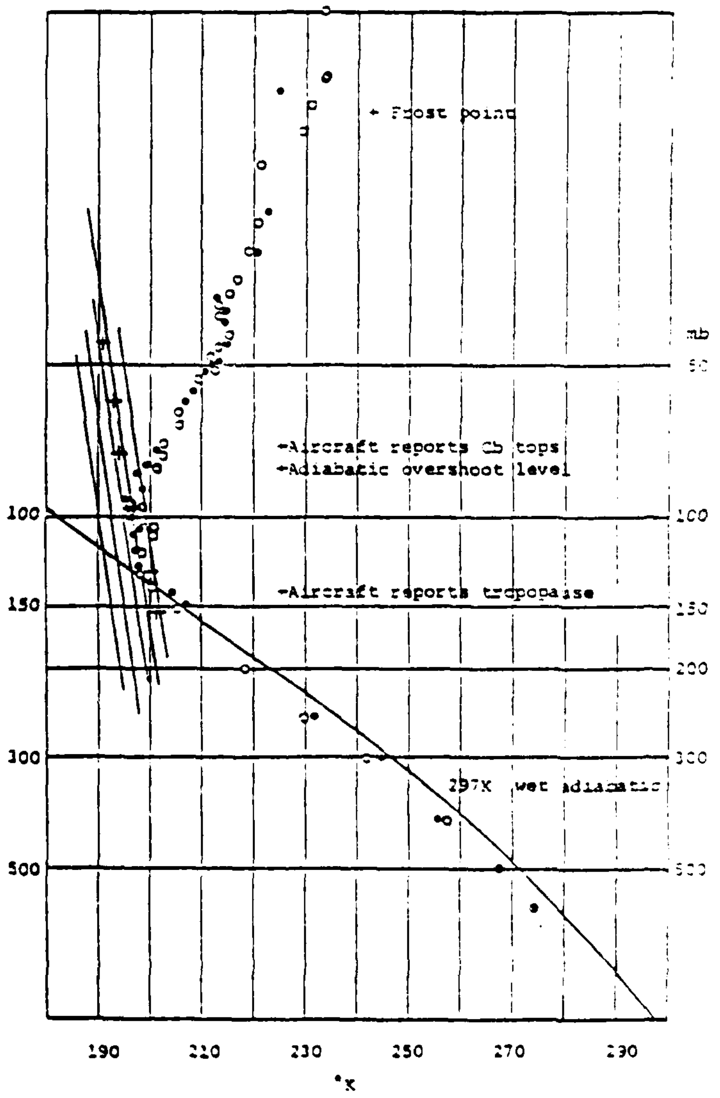


Fig. 3.13 Radiosonde temperature and aircraft humidity sounding.
Panama 31 July 1977

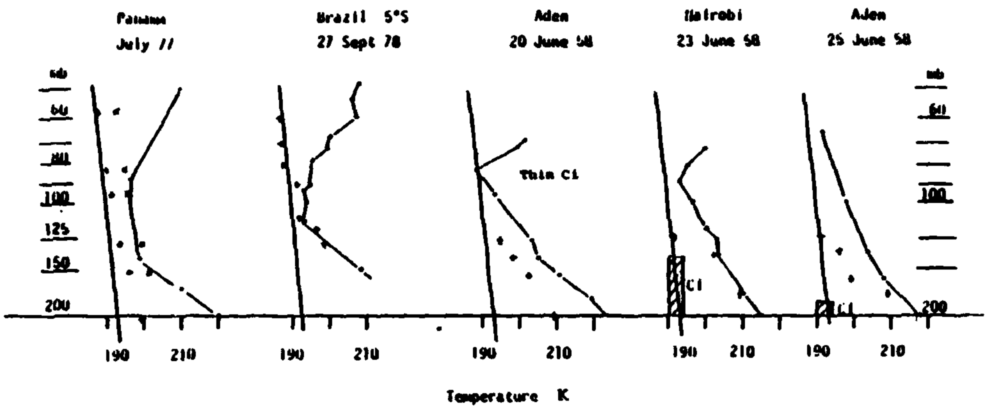


Fig. 3.14 Examples of temperature and frost-point structure near the tropical tropopause. The isopleth of saturation at mass mixing ratio 2×10^{-6} is shown.

3.4.4 Implications of the water content observations

This review has covered all the measurements of water content near the tropopause which have sufficient accompanying detail of vertical atmospheric structure to place them in the context of the mass transport hypothesis advanced in Section 3.3.2.

In temperate latitudes we find no observation of water content, higher in the atmosphere than about the 16 km - 100 mb level and made by a reliable method in circumstances clearly excluding contamination, which contradicts the hypothesis that air does not move upward through this level in these latitudes, but there are too few observations to establish it with a high degree of confidence.

The current interpretation of Brewer's freeze-dry mechanism (see Reiter *et al.* (1975), Chap. 3-3 and Robinson *et al.* (1975), Chap. 7) appears to be a global rising motion through the tropical tropopause effectively uniform over a hemispheric latitude band between 15° and 30°

wide with velocity at the tropopause of order 10^{-4} m sec^{-1} - the rising branch of the Hadley cell. Cloud and precipitation are essential factors in the freeze-dry mechanism. If air passing through the tropopause comes from the lower atmosphere, as is indicated by the windfield and required by the dynamic argument, the cloud must be thick cloud. A band 15° of latitude wide is certainly not filled with thick cloud. Even a high extensive veil of thick cirrus is observed on only about 25 percent of occasions, e.g., Kerley (1960): one tenuous enough to be observed with difficulty could only be produced by general ascent of air with an initial humidity very little greater than the stratospheric humidity of about $3x10^{-6}$- implying a mean toroidal circulation of shallow depth in the vicinity of the tropopause, recycling stratospheric air with a small turbulent admixture from the lower troposphere. This mechanism would satisfactorily explain the very low relative humidity frequently observed in the high subtropical troposphere. It would satisfy the radiative argument, but not the energy and mass budget. A possible alternative to general slow ascent is a substantial component of downward return flow of air which had ascended from the moist low troposphere in convective cloud towers: this would call for low upper tropospheric humidities between the towers. This explanation implies an ascending branch of the mean meridional circulation entirely confined to cumulus towers, with slow descent at all other locations in the upper tropical and subtropical troposphere. Since on this hypothesis the towers would be the only source of air for the region above the upper 'line' of Fig. 3.3, the humidity of the injected air could not exceed the general stratospheric humidity of about $3x10^{-6}$. A further note of caution is necessary. The arguments used were here assume the temperature-pressure-mixing ratio relationship of Table 1. We cannot be quite sure that this is appropriate to an equilibrium between the atmosphere and cloud ice particles at these temperatures, or even that the cloud processes are slow enough to allow equilibrium.

The Brewer mechanism thus calls for an atmospheric structure with saturation over a considerable depth of the troposphere up to a tropopause within the limits set out in Table 3.1 and with no subsequent significant decrease of water content higher in the stratosphere. There is no published observation which fits these criteria strictly, though some of Mastenbrook's (1968) observations at Trinidad probably do so within the limits of observing error. Some of the difficulties of detail are illustrated in the examples of Fig. 3.14. Of these Aden, 20 July 1958, meets the temperature-pressure criterion for the tropopause, with presumed saturation in the thin cirrus observed above the aircraft in dry clear air at 125 mb. The difficulty here is to explain the predrying of the upper tropospheric air, as is also the case for the 'dry' Panama observation of Fig. 3.12. The Brazil, September 1978, observation has a saturated tropopause, just within the range of Table 3.1, but the saturated layer is only 1.5 km thick. The difficulties are to explain the unsaturated troposphere below this layer, and the decrease of mmr with height in the stratosphere.

Mastenbrook (1968, 1974) drew specific attention to the fact that the tropopause criteria of Table 3.1 are frequently not met in tropical soundings. Table 3.5, derived from data in his 1968 paper, shows the frequency of occurrence of various tropopause saturation mmrs at Trinidad during the period of the measurements of Fig. 10. The criterion for saturation mmr 3×10^{-6} is rarely met in summer (May, June, July), but is met on about 50 percent of occasions in winter (Dec, Jan, Feb). In his 1974 paper, Mastenbrook exhibits plots of three-month running averages of tropopause saturation mmr. These plots must be interpreted with caution - for example, there is no three-month running average of mmr as low as 3×10^{-6} at Trinidad during the period when 50 percent of the individual values were lower than this. Nevertheless, the analysis shows that there must be many individual occasions in the Northern Hemisphere summer at the stations investigated (Trinidad, Panama, Kwajalein 9°N 168°E and Singapore 1°N 104°E) when even 3×10^{-6} saturation mmr is not reached. During the northern winter, values of 2×10^{-6} seem to be usual at Singapore, frequent at Kwajalein, and perhaps present on half the occasions at Panama. They appear to be rare at Trinidad. It is, therefore, particularly regretable that the only existing northern winter tropical observations of stratospheric humidity are at Trinidad. Although the observations of water content near the tropical tropopause do not establish the general slow ascent version of the Brewer mechanism, they clearly have not been made at the most appropriate places and times.

TABLE 3.5 Frequency of occurrence of saturation mass mixing ratio with respect to ice at the reported tropopause, Trinidad, W.I., 10°N-61°W in winter (Dec-Jan-Feb) and summer (May-June-July) 1964-1965.
(Mastenbrook, 1968)

	mmr x 10^6										
	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	>10
Summer	0	0	7	53	28	43	26	13	2	1	0
Winter	0	4	83	59	27	3	0	0	0	2	0

The alternative to the general slow ascent version is that the stratosphere is fed only by air which has ascended in cumulus towers reaching or exceeding the general tropopause height. A good example of 'adiabatic overshoot' was observed during the 1977 ITCZ expedition and is illustrated in Fig. 3.13. Adiabatic overshoot, as efficient as that implied by this observation, in turn implies an oscillation of the cloudy air with very little mixing, and the presence of an easily visible Cu head requires a high total H_2O content. The phenomenon is certainly not an obvious explanation of the dryness of stratospheric air, but it does raise the paradoxical possibility of dessication by injected ice particles, which might be supercooled in the overshoot process or by radiation to space or have an effective saturation vapor pressure lower than that used in Table 3.1. None of these speculations receives support from the 1977 Panama observations. The air between and above the cloud towers has the relatively high mmr appropriate to saturation at the tropopause. If this air remains in the stratosphere, it is not detected elsewhere -

the source must be small and in an environment providing for rapid turbulent mixing with air of mmr lower than the stratospheric average. The very few available observations lend no support to the 'convective cloud' version of the freeze-dry mechanism.

We conclude that whilst the broad features of stratospheric H_2O distribution and details of observations in temperate latitudes lead to a simple hypothesis concerning mass exchange between troposphere and stratosphere, examination of detail of the available tropical observations produces only difficulties. We turn for confirmation (or otherwise) to observations of other trace substances.

3.5 Exchange of other trace substances between troposphere and stratosphere

3.5.1 Application of the transport hypothesis

We have proposed that the minimum annual mass exchange between that part of the Northern hemisphere stratosphere above about the 100 mb level and the troposphere is 10^{17} kg, crossing the tropopause upward in the equatorial region and the 100 mb level downward poleward of the 'tropopause gap'. Any attempt to detail the dynamical processes which could effect this exchange meets with considerable difficulties. If the hypothesis proves useful, these difficulties must be faced: at this stage we ignore them. The minimum gross hemispheric transport of any material is 10^{17} kg yr^{-1} multiplied by the difference between the mmr at the tropical tropopause and that at about the 100 mb level poleward of the tropopause gap (or some weighted mean if the mmr at 100 mb varies with latitude). In a steady state situation, this net transport is equal to the stratospheric source or sink, which might be observable or calculable by other methods. In a transient situation, observations of changing atmospheric concentration and an inventory of sources and sinks should be consistant with the estimated troposphere-stratosphere transport. In following this approach, certain conventional assumptions will be made because of the paucity of observations. The southern and northern hemisphere mass transports will be taken as equal, in spite of considerable known differences in composition (e.g., O_3 content) and physical state. If the temperate latitude mmr is taken from a concentration field interpolated by other authors, the value at 16 km (or 100 mb) 50°N will be used. If there are differing observations at several seasons of the year in a transient situation, Northern Hemisphere observations in the first four months of the year will be chosen.

3.5.2 Stratospheric mass balance of the hydrogen species

The species concerned are H_2O, CH_4, HNO_3 and $HC\ell$. There is a surface source of CH_4, which observation shows to be well mixed in the troposphere. It is oxidized in the high stratosphere, producing H_2O and CO_2 through a complex of reactions (not including direct photolysis) which might also lead to the production of some H_2. H_2 appears to be reasonably well mixed through the troposphere and stratosphere, with a small decrease of mixing ratio with height. There may be a net loss of protons to space. There is no identified significant chemical sink of H_2O and we ignore the possible polar freeze-dry sinks because of the very restricted geographical areas and height ranges involved. Table 3.6 shows the application of our mass transfer hypothesis to the CH_4 observations. The earlier measurements in the stratosphere are not presented in the literature in a particularly suitable manner for this interpretation - they usually appear as means of several balloon ascents at levels referred to a presumably averaged tropopause, which is invariably very high. (Because of the logistics of operation of large balloons, these flights are most frequently made in the position corresponding to $Y'Y$ of Fig. 3.4.) In Table 3.6, line 1, the CH_4 mmrs are a subjective synthesis of the 1977 Panama expedition observation at the tropical tropopause with measurements made by D. Ehalt and his colleagues. (See, for example, 'Halocarbons', Fig. C12, p. 298), the judgement being that at 16 km 50°N, the mmr is ninety percent of the tropospheric mmr. The five balloon ascents for measurement of CH_4 concentration by Bush *et al.*, (1978) are presented in a manner which allows direct application of the mass transport hypothesis, and include one ascent (Laramie, WY, 14 February 1978), which is probably in a position corresponding to the line X´X of Fig. 3.4. The mmrs and mass transports indicated are in close agreement with line 1 of Table 3.6. Some recent measurements of CH_4 concentration at latitude 30 -40 N are shown in Fig. 3.15. In line 2 of Table 3.6, the mmrs are an indirect interpretation of Fig. 4 of Farmer *et al.*, (1974). Column 4 of Table 3.6 is the minimum annual gross transport of the species concerned through the equatorial tropopause, according to our hypothesis. The HNO_3 and $HC\ell$ entries are from Tables 3.7 and 3.8 of this report. At a 'Winter Course in Atmospheric Chemistry' held in January 1979, D. Ehalt presented a very detailed assessment of the hydrogen species mass budget which included a large tropospheric chemical sink of CH_4. His estimate of the net transport of CH_4 to the stratosphere was 2.5×10^{10} to 8.5×10^{10} kg yr^{-1} compatible with line 2 of Table 3.6, but 2 to 5 times the line 1 estimate, which is based on more direct and more numerous measurements of concentration.

TABLE 3.6 Stratospheric mass balance of the hydrogen species

	1	2	Column 3	4	5
Line	Species	Tropical Tropopause mmr	Temperate Tropopause mmr	Gross transport to Stratosphere (Global)	Net transport to Stratosphere (Global)
1	CH_4	3×10^{-7}	7.2×10^{-7}	1.6×10^{11}	1.6×10^{10} (4×10^{9}H)
2	CH_4	6.6×10^{-7}	4.4×10^{-7}	1.3×10^{11}	4.4×10^{10} (1.1×10^{10}H)
3	H_2O	(3×10^{-6})	(3×10^{-6})	6×10^{11}	(0)
4	HNO_3	1×10^{-11}	1.5×10^{-9}	2×10^{6}	-3×10^{8} (5×10^{6}H)
4a	HNO_3	(0)	7.5×10^{-9}	(0)	-1.5×10^{9} (2.5×10^{7}H)
5	$HC\ell$	(0)	1×10^{-10}	(0)	$- 2 \times 10^{7}$ (6×10^{5}H)

Figure 3.15 illustrates observations of the concentration of CH_4 in the 30 N-40 N latitude band, by various methods and at various seasons, at locations in the USA and Western Europe. The line is a modeled profile to which reference is made later (Section 3.7). Figure 3.16 contains details of two balloon ascents to measure H_2O concentration by the Lyman-α fluorescence technique (Kley *et al.*, 1979). There is no *a priori* reason to doubt the validity of any observation plotted in these two diagrams, which provide examples of the possible variability of the concentration of reactive species. The smoothed average of the measurements discussed by Harries (1976) is also shown on Fig. 3.16.

We can attempt to examine the fate of the CH_4 which enters the stratosphere with the aid of these diagrams and Table 3.6. The hydrogen in the CH_4 which is destroyed can be exported from the stratosphere only as H_2, $HC\ell$, HNO_3 and H_2O. The few existing measurements of H_2 concentration show that it varies only slowly with height, and there is no recognized tropospheric sink. The estimated loss of protons to space (Donahue, 1977) is the equivalent of about $2x10^8$ kg yr^{-1} of H_2O or $9x10^7$ kg yr^{-1} of CH_4. In Table 3.6 the loss of $HC\ell$ and HNO_3 to the troposphere is estimated at about the equivalent of about $2x10^8$ kg yr^{-1} of H_2O or $8x10^7$ kg yr^{-1} of CH_4. The chlorine and nitrogen species mass balances suggests that this number cannot be in error by a factor of more than about four. The losses to space and to the chlorine and nitrogen cycles are negligible in comparison with the minimum net CH_4 transport consistent with our hypothesis, which is $1.6x10^{10}$ kg yr^{-1}. If all the CH_4 contained in a parcel of air were destroyed, and the CH_4 volume mixing ratio at entry were about $1.5x10^{-6}$, the H_2O volume mixing ratio would be increased by about $3x10^{-6}$; the mmr by about $2x10^{-6}$. This is the maximum increase in H_2O concentration above that at entry which can be attributed to CH_4 destruction, since the CH_4 content of air entering the stratosphere does not vary appreciably, whatever the location and mechanism of entry.

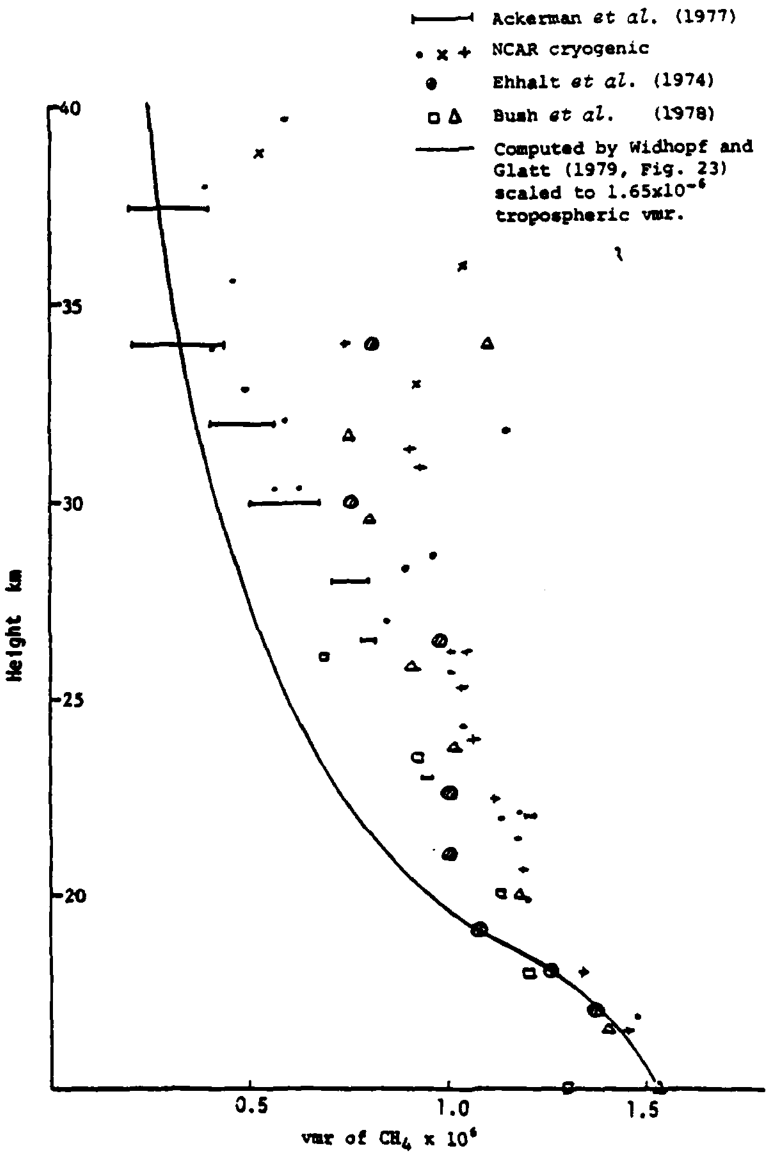


Fig. 3.15 Observations and computations of the concentration of CH_4 30°-40°N

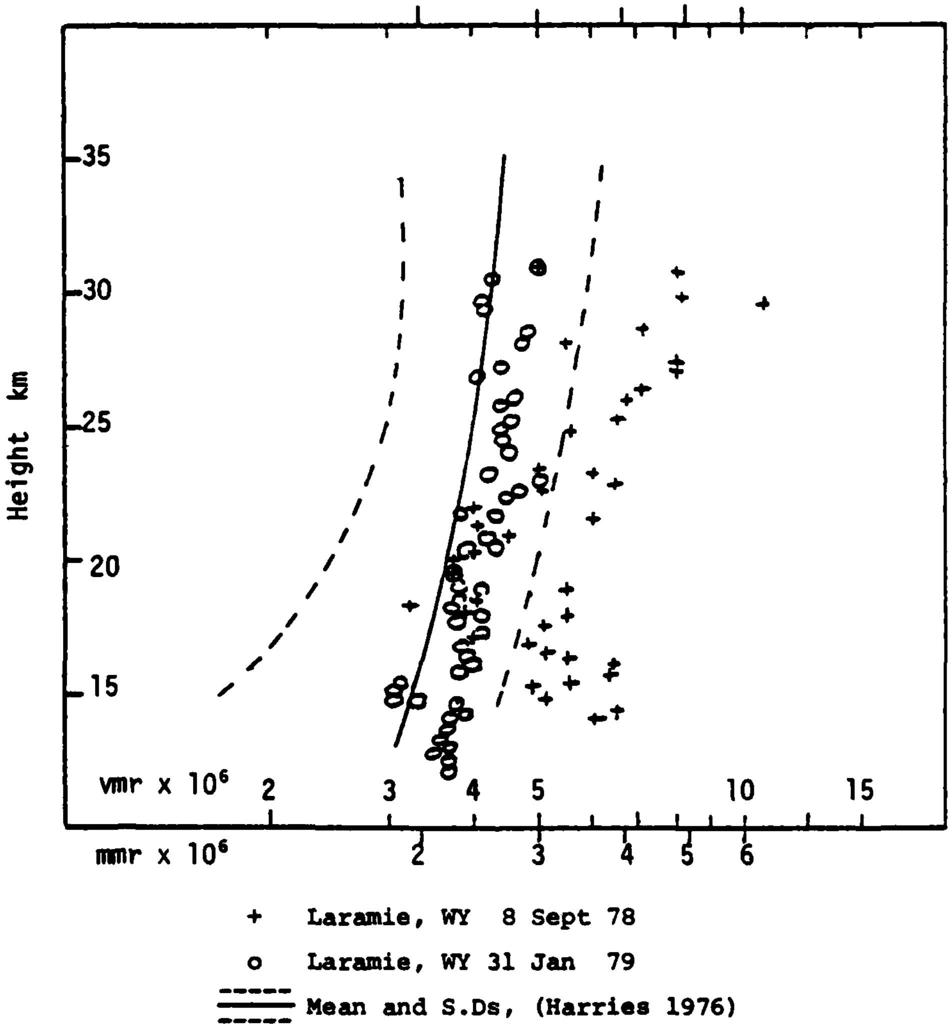


Fig. 3.16 Observations of the concentration of H_2O

According to Table 3.6, only one tenth of the CH_4 entering the stratosphere is destroyed, so that the average increase in the mmr of H_2O in air leaving the stratosphere is $2x10^{-7}$; 10 percent or less of the mmr at entry. There is no immediate prospect of securing sufficient observations suitably distributed in location and time of year, and of sufficient accuracy, to establish a change of this magnitude and confirm the transport hypothesis directly.

We may make a rough estimate of the mixing ratio of H_2O in the upper stratosphere by adding the H_2O equivalent of the local deficit of CH_4 to the average H_2O mmr at entry, so that according to Fig. 3.15 the mmr of H_2O at 35 km should be $0.5x10^{-6}$ to $1.3x10^{-6}$ greater than the average at entry into the stratosphere; at 25 km it should be about $0.5x10^{-6}$ greater than at entry. These numbers are in reasonable agreement with the observations plotted in Fig. 3.16, but do not, necessarily, confirm the transport hypothesis quantitatively since they depend on the ratio of H_2O and CH_4 concentration at entry, not on the total amount. If we accept the validity of the individual observations in Fig. 3.16, we have an indication of the variability of the H_2O mmr at entry into the stratosphere; for example, the point at 29.5 km on 8 September 78 (mmr $6.3x10^{-6}$) implies an H_2O mmr of at least $5x10^{-6}$ on entry; that at 28 km (mmr $3.3x10^{-6}$) at least $2.5x10^{-6}$ on entry.

3.5.3 Stratospheric mass balance of the nitrogen species

Some background knowledge of the nitrogen cycle will be assumed. Stratospheric aspects are treated in NAS/NRC (1977) 'Halocarbons', and the whole environmental nitrogen cycle in NAS/NRC (1978) 'Nitrates' and in Cothern (1979) and Bolin (1979). Nitrous oxide is released in biological processes at the surface. It appears to be relatively stable in the troposphere where it is well mixed but is removed by chemical reaction and photolysis in the stratosphere. The major nitrogenous product is N_2, but a proportion is converted to NO which is involved in numerous chemical reactions. The major sink of the 'odd' nitrogen, i.e., that initially converted to NO, is through HNO_3, which has a long enough life for some to reach the troposphere and be removed in the precipitation process. Some may also be similarly removed as NO_2. There is no recognized stratospheric sink of odd nitrogen below about 60 km. Purely from the point of view of the stratospheric nitrogen balance, industrial and surface transportation sources of odd nitrogen may at present be ignored.

Table 3.7 shows the results of application of our transport hypothesis to this problem. The sources of the mmrs used: N_2O, line 1, Column 2, the 1977 Panama ITCZ expedition, Column 3, R. E. Newell (1979) - a privately communicated interpolation of aircraft measurements, reading at 50°N 16 km adopted. HNO_3, line 2, Columns 2 and 3, Lazrus and Gandrud, reported in 'Halocarbons' Fig. 7.7; HNO_3, line 3, Column 2, Lazrus and Gandrud, Column 3 Harries *et al.* and Fontanella *et al.* reported in 'Halocarbons' Fig. 7.7. Odd N, line 4, Column 2, no measurement available, Column 3, Evans *et al.* (1978).

TABLE 3.7 Stratosphere-troposphere interchange of the nitrogen species.

	Column 1	Column 2	Column 3	Column 4
Line	Specie	Tropical Tropopause mmr	Temperate Tropopause mmr	Global Net Transport to Stratosphere kg yr^{-1}
1	N_2O	$5x10^{-7}$	$4.2x10^{-7}$	$1.6x10^{10}$ $(1x10^{10}N)$
2	HNO_3	$1x10^{-11}$	$1.5x10^{-9}$	$-3x10^{8}$ $(-6x10^{7}N)$
3	HNO_3	(0)	$7.5x10^{-9}$	$-<1.5x10^{9}$ $(-<3x10^{8}N)$
4	Odd N	(0)	$1x10^{-9}$	$-<2x10^{8}N$

The first direct inference that can be drawn from Table 3.7, dividing the total atmospheric content of N_2O by the annual loss, is that the average life of an N_2O molecule in the atmosphere is 150 years. The second is that if the Lazrus-Gandrud mixing ratios are correct, only 0.6 percent of the N_2O destroyed in the stratosphere is exported as HNO_3. If the Harries *et al.* mixing ratios are correct, the proportion is almost three percent. The Evans *et al.* measurements of total odd nitrogen indicate that, at most, two percent of the N_2O destroyed is exported in this form.

Four apparently independent empirical estimates of the N_2O flux to the stratosphere have been located. Robinson and Robbins (1975) find a net flow of $3.8x10^{10}$ kg yr^{-1} N_2O ($2.4x10^{10}$ kg yr^{-1} N) with $5x10^{9}$ kg yr^{-1} ($3.2x10^{9}$ kg yr^{-1} N) converted in the stratosphere to NO_x, the remainder to N_2. 'Nitrates' (p.22) suggests a surface source of $2x10^{10}$ kg yr^{-1} N_2O and an additional atmospheric source (specified cryptically as from N_2 via O_3) of $1.5x10^{10}$ kg yr^{-1}. The total is effectively the same as that of Robinson and Robbins. In each case $5x10^{9}$ kg yr^{-1} N_2O (about fifteen percent of the net flux to the stratosphere) is converted to NO_x ($3.2x10^{9}$ kg yr N). The two mass balance estimates yield the same NO_x production. A reading of 'Nitrates' does not, however, produce much confidence in the mass balance estimates. Cothern (1979), Table IV, p.58, (apparently placing considerable reliance on estimates by Hahn and Junge), gives the 'likely value' for total N_2O production as $1.4x10^{11}$ kg yr^{-1} with a range from $3x10^{10}$ to $5x10^{11}$, and a 'likely' stratospheric destruction of $2x10^{10}$ kg yr^{-1}, range $1x10^{10}$ to $4.5x10^{10}$. Bolin (1979), with all the above material at his disposal, estimates the stratospheric destruction as $1.5x10^{10}$ kg yr^{-1}, range 0.9 to $2.0x10^{10}$.

It thus appears that the earlier estimates of total N_2O destruction suggest a mass transport to the stratosphere of 2 to 2.5 times the minimum of our transport hypothesis, whereas later estimates (Cothern and

Bolin, both apparently relying heavily on the work of Hahn and Junge), are consistent with our minimum value. Because of the impossibility of identifying the N_2 produced by photolysis, the estimates of odd N production which follow from our hypothesis cannot be used as quantitative confirmation, except indirectly using arguments employing atmospheric models. This aspect of the N_2O and odd N observations is considered in Section 3.6. So far as the concentration measurements are concerned, there is a significant unresolved difference between those relying on chemical (filter) sampling and those employing spectroscopic analysis techniques. The full application of our transport hypothesis, which might also allow an assessment of the importance of surface sources of pollutant odd N, is hindered by the paucity of measurements of HNO_3 and odd N near the tropical tropause.

3.5.4 Mass balance of the chlorine species

Some knowledge of the background to this problem, e.g., as set out in 'Halocarbons' (NAS/NCR (1976)) will be assumed. Certain halogenated hydrocarbons which are released into the atmosphere during industrial and domestic activity are extremely stable in the atmosphere below a level around 30 km, above which they are destroyed by chemical reaction and photolysis. In the subsequent complex of reactions, some $HC\ell$ is formed: This has a long enough lifetime to be partially returned to the troposphere where it is removed in precipitation. This is the only identified sink of stratospheric chlorine. The atmospheric concentration of all the compounds concerned is observed to be rising; the steady state has not been reached. The release rates are reasonably well known from production statistics. There are, in addition, certain less stable halogenated hydrocarbons with both artificial and natural sources but little is known in detail of their fate in the atmosphere. It is generally assumed that the chlorine ion originating in sea salt is removed in the troposphere by the precipitation process. Table 3.8 contains data on the three major very stable compounds. There is no reason to expect any natural source of the two fluorinated compounds (CFMs). The question of a natural source of $CC\ell_4$ appears to be open but the possibility will be ignored initially. Columns 2 and 3 of Table 3.8 are derived from production statistics ('Halocarbons', pp. 39, 43). The $CC\ell_4$ estimate reflects decreased U.S. production by 10^8 kg yr^{-1} between 1971 and 1973, which has been presumed proportionally applicable to global production. Columns 5 and 7 are derived from these numbers by assuming negligible destruction and efficient mixing of the three compounds during the period of major release (10 years). Column 7, transport to the stratosphere, is thus simply one-eighth of the annual release rate, this being approximately the stratospheric proportion of total atmospheric mass. Columns 4, 6 and 8, to be compared with Columns 3, 5 and 7, are from the observations of concentration compiled by Singh *et al.* (1979) entries in Column 8 being one-eighth part of those in Column 4. Columns 9, 10 and 11 are an application of our mass transfer hypothesis. The sources of the mmrs used are: $CFC\ell_3$, line 1, Column 9, measurements made by D. Cronn of Washington State University near Panama during the July 1977 ITCZ expedition; line 1, Column 10, 'Halocarbons', Fig. 6.1 scaled to the 1977 Panama data; line 2, Columns 9 and 10, Krey *et al.* (1977), $CF_2C\ell_2$, line 3, Column 9, Panama 1977 (D. Cronn); line 3, Column 10, no suitable temperate tropopause measurements of $CF_2C\ell_2$ were located. $CC\ell_4$, line 4, Column 9, Panama 1977 (D. Cronn); line 4, Cloumn 10, Krey *et al.* (1977), scaled to the Panama measurement; line 5, Columns 9 and 10, Krey *et al.* (1977). $HC\ell$, line 6, Column 9, no suitable measurement located; line 6, Column 10, subjective average from 'Halocarbons' Fig. 6.6.

Table 3.8 shows that in the case of $CFC\ell_3$ and $CF_2C\ell_2$, the observed global mmr and its rate of increase are in accord with the no destruction assumption, and that the troposphere to stratosphere transport deduced from our mass transfer hypothesis agrees with the release rate and the no destruction assumption. In the case of $CC\ell_4$, interpretation is complicated

TABLE 3.8 Mass balance of the chlorine species.

	Column 1	2	3	4	5	6	7	8	9	10	11
Line	Specie	Total release to 1975	Release rate 1975	Rate of increase 1975/1977 (Singh et al.)	Global average mmr 1976 (no destruction)	Global average mmr 1976/77 (Singh et al.)	Transport to stratosphere (no destruction & Col 3)	Transport to stratosphere (no destruction & Col 4)	Tropical tropopause mmr	'Temperate tropopause mmr	Global net transport to stratosphere
		kg	kg yr^{-1}	kg yr^{-1}			kg yr^{-1}	kg yr^{-1}			kg yr^{-1}
1	$CFCl_3$	$3x10^9$	$3x10^8$	$2.8x10^8$	$6x10^{-10}$	$5.5x10^{-10}$	$3.7x10^7$	$3.5x10^7$	$7x10^{-10}$	$5x10^{-10}$	$4x10^7$ ($2.3x10^7$Cl)
2	$CFCl_3$								$4.8x10^{-10}$	$3.3x10^{-10}$	$3x10^7$ ($1.7x10^7$Cl)
3	CF_2Cl_2	$4.5x10^9$	$3.5x10^8$	$3.8x10^8$	$9x10^{-10}$	$8.8x10^{-10}$	$4.4x10^7$	$4.7x10^7$	$1x10^{-9}$	-	-
4	CCl_4	$4.1x10^9$	$5x10^7$	$6x10^7$	$8x10^{-10}$	$6x10^{-10}$	$6.3x10^6$	$7.5x10^6$	$6x10^{-10}$	$4.4x10^{-10}$	$1.2x10^7$ ($2.2x10^7$Cl)
5	CCl_4								$4.6x10^{-10}$	$3.4x10^{-10}$	$2.4x10^7$ ($2x10^7$Cl)
6	HCl								(0)	$1x10^{-10}$	- $<2x10^7$ ($-<2x10^7$Cl)

by the major adjustment of release rate in the early 1970's. The observed global average mmr is 75 percent of that expected on a no destruction assumption - a marginally significant difference. The transport to the stratosphere in 1975-1977 computed from our hypothesis is approximately half the release rate for those years.

The HCℓ transport in Table 3.8 accounts for at most one-third of the Cℓ entering the stratosphere on the 'no destruction' assumption, and rather less than half the contribution of $CFC\ell_3$ + $CC\ell_4$ according to our mass transport hypothesis. It accounts for, at most, one-twenty-fifth of the total Cℓ released in $CFC\ell_3$, $CF_2C\ell_2$ and $CC\ell_4$ - a mean residence time for the three species of more than 25 years, if there is no other stratospheric Cℓ source. There is almost certainly an atmospheric chlorine source connected with $CH_3CC\ell_3$ of magnitude comparable with that due to $CFC\ell_3$, but available observations do not allow its partition between stratosphere and troposphere. To the extent that it is stratospheric, it would increase this estimate of residence time of the CFMs + $CC\ell_4$ probably to more than 50 years. The HCℓ transport could lie between one-third times and three times that of Table 3.8 because of uncertainty in the mmr. With the precision of the data used, there is no question of distinguishing a 25-year average life from 'no destruction'. However, Table 3.8 suggests that $CC\ell_4$ has a significantly shorter average life than the CFMs and that its global concentration has passed the initial linear stage of the growth curve and may now be exhibiting transient adjustment to the 1971-1973 production decrease.

In summary, the transport hypothesis on which Column 11 of Table 3.8 is based is consistent with data concerning the release, growth rates, and distribution in the atmosphere of the halocarbons, and with current theories concerning their destruction and eventual removal from the atmosphere. The actual stratosphere-troposphere mass exchange required is about the minimum exchange compatible with the hypothesis, but there are major uncertainties, at least a factor of two, stemming from uncertainties in the HCℓ concentration, and the lack of published near-tropopause measurements of the concentration of other chlorinated hydrocarbons, particularly $CH_3C\ell$ and $CH_3CC\ell_3$.

3.5.5 Tropospheric mass balance of ozone

There are probably sufficient ozone soundings of good quality to allow the mass transport hypothesis to be applied with more precision than for any other substance. The result of such a test would be the annual export of ozone from stratosphere to troposphere. Table 3.9 is an approximate treatment. The mmr in line 1 is the spring 50°N 100 mb value read from a diagram due to Dutsch (1978) and that in line 2 is from a tabulation appropriate to mid-latitudes produced by Krueger and Minzner (1976). Conventional estimates of the net O_3 *transport from stratosphere* to troposphere are attempts to quantify O_3 destruction at the surface and vary widely from about 2.5×10^{11} to 1.5×10^{12} kg yr^{-1}. This range is commensurate with the estimates of Table 3.9, given the existence of a tropospheric ozone source of unknown magnitude, which eliminates the possibility of estimating the actual, rather than the minimum, value of the troposphere-stratosphere mass exchange from the O_3 concentrations and our hypothesis.

TABLE 3.9 Stratosphere-troposphere interchange of O_3

	Column			
	1	2	3	4
Line	Specie	Tropical Tropopause mmr	Temperate Tropopause mmr	Gross Transport to Stratosphere kg yr^{-1}
1	O_3	3×10^{-7}	2.0×10^{-6}	-1.4×10^{11}
2	O_3	3×10^{-7}	1.4×10^{-6}	-2.2×10^{11}

3.5.6 Stratospheric budget of contaminant carbon-14

Johnston *et al.* (1976) examined some aspects of the budget of C14 produced by nuclear weapons testing in the northern hemisphere stratosphere. Their main concern was to produce a consistent set of eddy diffusivities suitable for use in one-dimensional chemistry/transport models of the atmosphere, and they made, and published in detail, an interpolation of aircraft samples on a grid of points at 1 km height separation and 10° latitude separation from 8 to 29 km, 80°N to 30°S, each January from 1963 through 1965. In Table 3.10 we apply the mass transport hypothesis to the interpolated concentrations at 16 km 50°N and 16 km 0°. Column 5 of Table 3.10 is the total stratospheric content obtained by integrating the concentration tables with weighting according to zonal area. The transport estimated from our hypothesis using the minimum hemispheric mass exchange of 1×10^{17} kg yr^{-1} agrees reasonably well with the differences in total content from year to year. Johnston *et al's* interpolations can be accepted with reasonable confidence below 20 km, but at higher levels observations are sparse - the total stratospheric content entries are the least reliable 'observations' in Table 3.10 which is, therefore, not obviously inconsistent with the transport hypothesis.

TABLE 3.10 Decay of the Carbon-14 content of the stratosphere 1963-1965

		Column			
1	2	3	4	5	6
Date	C14 Mixing Ratio 50°N 16 km atoms kg^{-1}	C14 Mixing Ratio 0° 16 km atoms kg^{-1}	Transport to Troposphere atom yr^{-1}	Total Stratospheric C14 Content atoms	Decrease in C14 Content atoms yr^{-1}
Jan 1963	1.13×10^{11}	6×10^{9}	1.1×10^{28}	3.2×10^{28}	1×10^{28}
Jan 1964	6.02×10^{10}	9.4×10^{9}	5.1×10^{27}	2.2×10^{28}	8.5×10^{27}
Jan 1965	3.07×10^{10}	5.1×10^{9}		1.35×10^{28}	

3.6 Modeling the nitrogen species' mass balance

In Section 3.5.3 we compared the estimates of the stratospheric sink of N_2O based on our transport hypothesis with others prepared mainly from observations of the distribution of nitrogen species in the atmosphere. In this section the comparison is extended to include estimates of both the sink of N_2O and the odd nitrogen source prepared by operating chemical/transport models. The comparison is summarized in Table 3.11 which repeats certain entries from Table 3.7.

So long as we are concerned only with the total odd N content, the chemistry involved is fairly simple since there is no chemical sink, i.e., no reconversion to N_2O or N_2, at least below about 60 km. In the statistically steady state all the odd N formed must be removed by precipitation processes in the troposphere. The initial odd N specie is NO. The chemistry employed in the models represented in Table 3.11 is -

(a) $N_2O + h\nu \rightarrow N_2 + O(^1D)$ $\lambda < 230$ nm
(b) $N_2O + O(^1D) \rightarrow NO + NO$
(c) $N_2O + O^1(D) \rightarrow N_2 + O_2$
(d) Quenching of O^1D by N_2 and O_2
(e) Production of O^1D by $O_3 + h\nu \rightarrow O_2 + O(^1D)$

(McConnell and McElroy (1973) are also concerned with NH_3 oxidation as a source of odd N in the lowest layers of the stratosphere. This possibility has been neglected throughout this report in view of the absence of confirmed observation of significant NH_3 concentration in the upper troposphere. Line 8 of Table 3.11 refers only to the N_2O source.)

3.6.1 Estimates by Schmeltekopf *et al.*, (1977)

The basis of this work is a series of observations of N_2O concentration at various sites and times, up to a height of about 30 km. For the computations the observations must be extrapolated up to about 45 km

TABLE 3.11 Summary of estimates of the stratospheric sink of N_2O and source of odd nitrogen (expressed as kg yr^{-1} of nitrogen).

	Method	Source	N_2O Sink	NO Source	NO/N_2 Ratio
1.	Transport hypothesis and observed concentrations	Table 3.7, this report	$1x10^{10}$	$6x10^7$-$3x10^8$	0.006 to 0.03
2.	Mass balance	Robinson/Robbins	$2.5x10^{10}$	-	0.13
3.	Mass balance	"Nitrates"	$2.4x10^{10}$	-	0.15
4.	Mass balance	Cothern	$7x10^9$-$3x10^{10}$	-	-
5.	Mass balance	Dolin	$6x10^7$-$1.4x10^{10}$	-	-
6.	Chemical model and observed concentration	Schmeltekopf *et al*	$1.6x10^{10}$	$1.6x10^9$	0.10
7.	One-Dimensional model	McElroy and McConnell	$4.5x10^9$-$6.0x10^9$	$8.5x10^7$-$2.5x10^8$	0.02 to 0.04
8.	One-Dimensional model	McConnell and McElroy		$1.1x10^8$-$3.3x10^8$	
9.	Three-Dimensional model	Levy *et al*	$1x10^{10}$		[0.07 ??]

or to where the N_2O concentration becomes very small if this is below 45 km. Computation of the photodissociation calls for assumptions concerning solar output and the O_3 content above the level concerned. The computation is also sensitive to details of the structure of O_2 absorption. The authors estimate an overall uncertainty of their photodissociation rate as ± 50 percent. Computation of the $O(^1D)$ dissociations, reactions (b) and (c), calls for $O(^1D)$ concentration as a function of altitude, and the authors take this from the output of a two-dimensional model (due to Crutzen). The flux of N_2O through any level is the integrated destruction down to this level. The N_2O sink entry in line 6 of Table 3.11 is an area-weighted average of the total destruction computed for each N_2O profile. The NO_x production of line 6, Table 3.11, is an average, similarly area-weighted, of the reaction (b) computation. It, therefore, depends only on the Schmeltekopf *et al.* observations of N_2O concentration, Crutzen's two-dimensional model $O(^1D)$ profile, and the assumed rate constant of reaction (b). The whole process does, of course, assume that the observations as a set are representative of conditions over the globe and through the year. It should be noted that these computations of both the N_2O destruction and the NO_x formation are heavily weighted by a single tropical ascent which shows very high values of N_2O concentration (i.e., $>2\times10^{-7}$ by volume) up to 30 km, and by its very speculative upward extrapolation.

3.6.2 The estimate of McConnell and McElroy (1971, 1973)

This was pioneering work in the area and was completed before the standardization of reaction rates, quantum yields, and to some extent eddy diffusivity profiles, which characterized the CIAP process. The numbers in Table 3.11 are extracted from two papers; line 7 from McElroy and McConnell (1971) and line 8 from McConnell and McElroy (1973). The second paper incorporates a comprehensive chemical scheme (without the chlorine compounds). In both papers a standard O_3 profile based on observation was assumed. Two N_2O photolysis reactions were considered.

$$\begin{aligned} N_2O + h\nu &\rightarrow N_2 + (O^1D) \\ &\rightarrow NO + N \end{aligned}$$

with the caution that 'there is no definitive evidence' that the second is significant in the atmosphere. The procedure was to assume an N_2O concentration in the troposphere (from observation), to assume a K profile, and to postulate the flow of N_2O (zero) and odd nitrogen at an upper boundary.

The estimates in line 7, Table 3.11, are produced by manipulation of the information contained in Fig. 1 of the 1971 paper. The NO source is taken directly from Fig. 1b at the 15 km level. The N_2O sink is computed as the flow through the 15 km level given by the gradient of the N_2O concentration curves in Fig. 1a multiplied by the appropriate K. The values quoted correspond to $K = 10^3$ cm^2 sec^{-1} and $K = 10^4$ cm^2 sec^{-1}. The tropospheric N_2O volume mixing ratio was taken in both papers to be 2.5×10^{-7} and in Table 3.11 the originally derived line 7 and line 8 values have been multiplied by a factor 1.2 so that they are directly comparable to other entries based on a tropospheric vmr $\sim 3 \times 10^{-7}$.

3.6.3 Estimates by Levy, Mahlman and Moxim (1979)

These authors employ a version of the GFDL three-dimensional tracer model on a ~265 km grid with eleven levels, four of them above 15 km standard height. The chemistry is reactions (a) to (e), assuming the observed annual mean O_3 profile. The procedure was to assume a surface mixing ratio for N_2O (2.95×10^{-7} vmr), to run the model and adjust the N_2O flux at the surface to maintain this mixing ratio. In addition to this source (1×10^{10} kg yr^{-1} nitrogen equivalent), the paper exhibits zonal mean N_2O distributions for summer and winter and the corresponding standard deviations. The partition between N_2 and NO, implicit in the computation, is not displayed in the paper. (Mahlman-personal communication, 1979 - confirms that this information is currently being extracted and makes a tentative estimate of 0.07 for the NO_x/N_2 ratio expressed as N. This number should not be quoted without reference to GFDL.)

3.6.4 Comments on Table 3.11

Keeping in mind the assessment by Schmeltekopf *et al.* that uncertainties of the photon fluxes used in computing the N_2O photolysis may amount to ± 50 percent, the estimates of the N_2O sink in Table 3.11 are in reasonable agreement, with the exception of the two early mass balance estimates, lines 2 and 3.

This situation concerning the odd nitrogen source is much less satisfactory, with entries over a tenfold range. The magnitude of the source is an important factor in the understanding of atmospheric chemistry and the interplay of transport and reaction terms in the models. It is implicitly contained in all models of the unperturbed atmosphere but is usually not explicitly extracted, model verification being displayed in terms of concentrations and their variation with location, season and height.

The preliminary indications of Table 3.11 are, however, either that the transport hypothesis applied in line 1 underestimates the NO_x/N_2 ratio in the destruction of N_2O, or that the model computations of this ratio are too high. Looking in turn at these possibilities, we note that application of the transport hypothesis to determination of the N_2/NO ratio does not involve the absolute magnitude of the mass transport. The result depends entirely on two or three measurements of NO_x or HNO_3 content in the lower temperate stratosphere which cover a wide range. The data do, however, include the measurements of the NO_x species by Evans *et al.* (1978) to which further reference is made below. These measurements tend to support the upper limit of the line 1, Table 3.11, ratio estimate. The major uncertainty with the line 6 estimate is the extrapolation of the measurements above 30 km. Examination of Figs. 6 and 10 of Schmeltekopf *et al's* paper shows that one-third of the NO_x production in temperate latitudes and more than one-half the production in the tropics occurs above 30 km in the extrapolated region of the N_2O profile. Similar considerations apply to the Levy-Mahlman-Moxim result: the top level of their model is at 31.4 km, and the vertical resolution at the top layer about 9 km. The relatively high concentration of N_2O at the upper limit of their model (see Figs. 3.18 and 3.19) also suggests that the total N_2O destruction, as well as the NO_x/N_2 partition ratio, must depend considerably on upward extrapolation and may not be reliably computed (though it agrees with the transport hypothesis estimate).

Of the models considered in Table 3.11, only the two one-dimensional models extend above 30 km, and their results for mass balance and NO_x/N_2 ratio are commensurate with the line 1 estimate from the transport hypothesis. It is unfortunate that mass balance estimates have not been extracted from the three comprehensive two-dimensional models with up-to-date chemistry (Ames, Aerospace, NCAR) which have been applied to the FAA aircraft emissions problem. Results from the application of these models to the unperturbed atmosphere have been mainly displayed in terms of concentration profiles, some of which are displayed below (Section 3.7).

3.7 Modeling the nitrogen species concentration

In Section 3.6 some doubts were raised concerning the rate of production of odd nitrogen species from N_2O. This quantity does not enter directly into chemical models - local concentration is required and is is normally displayed and used in verification. Local concentration is related to the divergence of mass flux: it is, in principle, possible to model the concentration of any specie correctly with an incorrect total mass flux, but in this case the concentration of other species might not be correctly modeled and, specifically, the influence on concentrations of a perturbation of mass flux might not be correctly modeled. In this section some aspects of this question will be discussed in relation to three models - the one-dimensional models of McConnell and McElroy, the three-dimensional model of Levy, Mahlman and Moxim, and the two-dimensional 'Aerospace' model, in variants described by Widhopf (1975), Glatt and Widhopf (1978), Widhopf and Glatt (1979) and in Hidalgo (1978). The main purpose of the examination is to look for guidance in the planning of future observing programs. The diagrams used in this section should not be regarded as definitive - most have been constructed by interpolation in published small-scale diagrams, rather than by seeking access to digital material not available in published form.

Figure 3.17 contains measurements of N_2O volume mixing ratio measured at locations between 30°N and 40°N, covering all seasons of the year. The sources are Schmeltekopf *et al.* (1977), Newell (1979) and Fig. 22c of Widhopf and Glatt (1979). The modeled profiles are from Widhopf (1975) Fig. 4, from Widhopf and Glatt (1979), Fig. 22c, for the 30°N profile, and from Hidalgo (1978), Tables 4 and 5, for the 40°N profile. The 1975 model contained a transport parameterization based on thermodynamic arguments and wind observations. In the 1978-79 model this parameterization was modified in two stages by reference to trace species observations. The first and major adjustment accommodated the C14 observations, which we noted in Section 3.5.6 as being in conformity with our transport hypothesis. The second adjustment was made to give a better simulation of the high-level N_2O concentration observations. The major difference between the chemistry of the 1975 model and the latest version of the 1978 model was inclusion in the latter of the Howard-Evenson determination of the rate coefficient of the reaction $HO_2+NO \rightarrow OH+NO_2$. This change should have only a minor effect on the primary N_2O photolysis and on the $O(^1D)$ concentration. (Hidalgo (1978) presents his Table 5 as the ratio between the concentrations of various species in versions of the Aerospace model differing only in the rate coefficient of the HO_2-NO reaction. Internal evidence in Widhopf and Glatt (1979) suggests, however, that the final adjustment to the Ks was also made between the two computations on which Hidalgo's tables are based, and that this, not the new rate constant, was the cause of the major changes in computed concentration above 27 km shown in Hidalgo's Table 5.)

Figure 3.18 contains profiles of the N_2O concentration at 40°N computed using the models included in Table 3.11, together with the two-dimensional profile for 40°N from Fig. 3.17. Reference to Fig. 3.17 shows that the available concentration observations do not allow any discrimination between the models, and do not in themselves contribute to resolution of the differences in modeled mass balance. In Fig. 3.15 the CH_4 profile for 40°N computed by the latest version of the Aerospace model is plotted together with the observations. (The source of the profile is Widhopf and Glatt (1979) Fig. 23, but all values have been multiplied by 1.2, as approximate normalization to the tropospheric CH_4 vmr of $\sim 1.5 \times 10^{-6}$ used elsewhere in this report.) The CH_4 measurements confirm the impression of very considerable variance given by the N_2O observations, and are even less convincingly modeled.

A notable feature of the observations displayed in Figs. 3.15 and 3.17 is the large variability from set to set at any level, particularly between 25 and 35 km. (In both these diagrams an attempt has been made to eliminate differences in sensor sensitivity by approximate reduction to a common tropospheric concentration.) Neither CH_4 nor N_2O would be expected to show appreciable diurnal concentration variation at these heights, and the modeled seasonal variations are of order 5 percent at latitudes 30°N to 40°N. Levy, Mahlman and Moxim (1979) computed the variance of daily averages of N_2O concentration; their model averages over the layer between 22.3 and 31.4 km. The variance of the individual observations in Fig. 3.17 is about 25 times the variance of the average for this layer computed by the three-dimensional model. If the observations are taken to be representative of a certain depth in the atmosphere, and we assume a representative sample, the spatial scale of the vertical structure necessary to reconcile the observations with the three-dimensional computation is only about 200 m. If rather more than half the observed variance is attributed to measurement error, the structure must have a vertical scale of about 1 km with a vmr amplitude of ± 30 ppmv. The number and resolution of available measurements is not sufficient to support or validate this kind of speculation.

Figure 3.19 illustrates N_2O concentration profiles at 10°N. There are very few observations; they are reasonably well simulated by the three-dimensional model, but not by the one-dimensional and two-dimensional models examined. Note that the Aerospace two-dimensional model profile illustrated here is from Fig. 4 of Widhopf (1975) and incorporates the unmodified thermodynamic transport parameterization. No tropical profile from the 1978 version with modified transport parameterization is available. Each model appears to underestimate the concentration.

Finally, Fig. 3.20 illustrates some profiles of total odd nitrogen concentration. With only one set of observations available, no useful comment can be made. The agreement between the Aerospace model profile and these observations is very close, but it is much less close for individual odd nitrogen species. Relative to observations the model overestimates the total column of HNO_3 by a factor of 2 to 3 at all latitudes, with corresponding low estimates of NO_2: these observations are, however, made by a single spectroscopic method and it is not unconceivable that they have a systematic error.

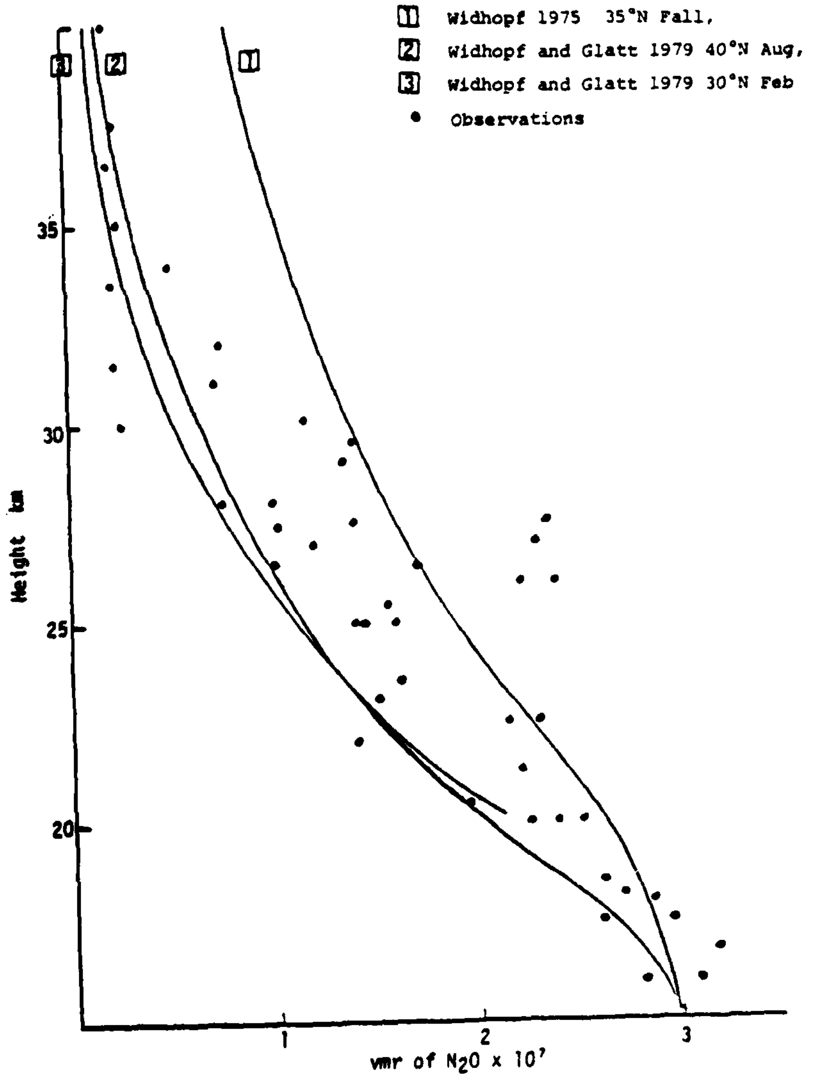


Fig. 3.17 Observations and computations of the concentration of N_2O 30°-40°N

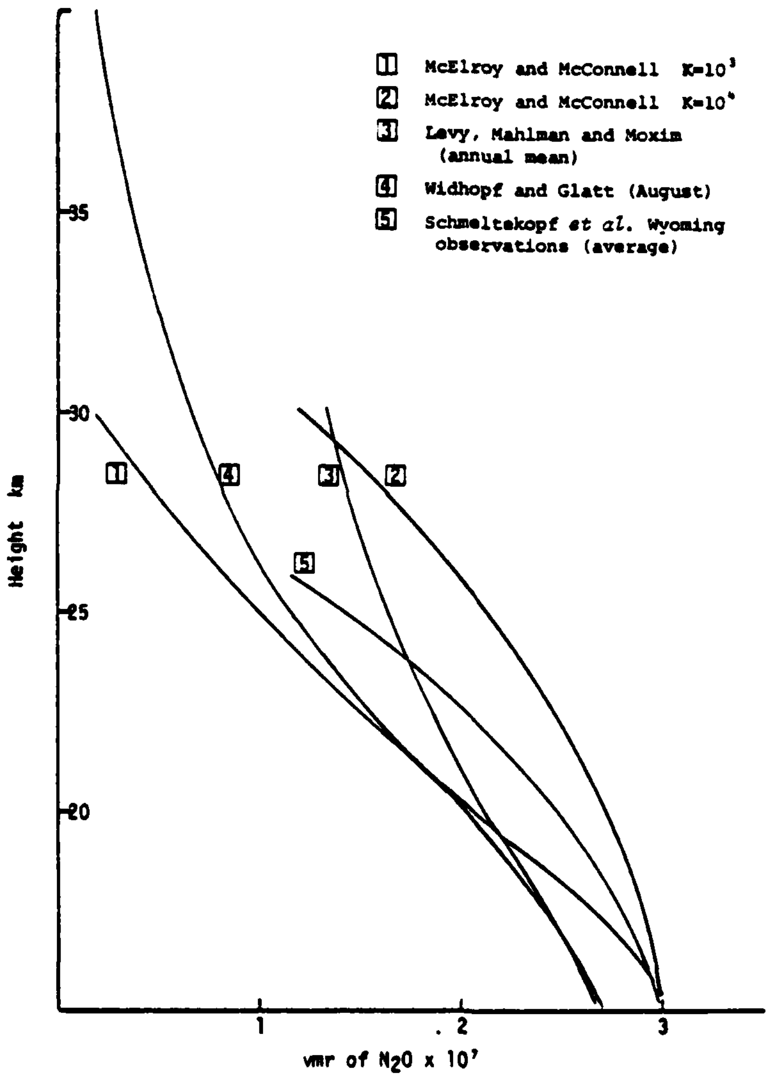


Fig. 3.18 Computations and observations of the concentration of N_2O, 40°N

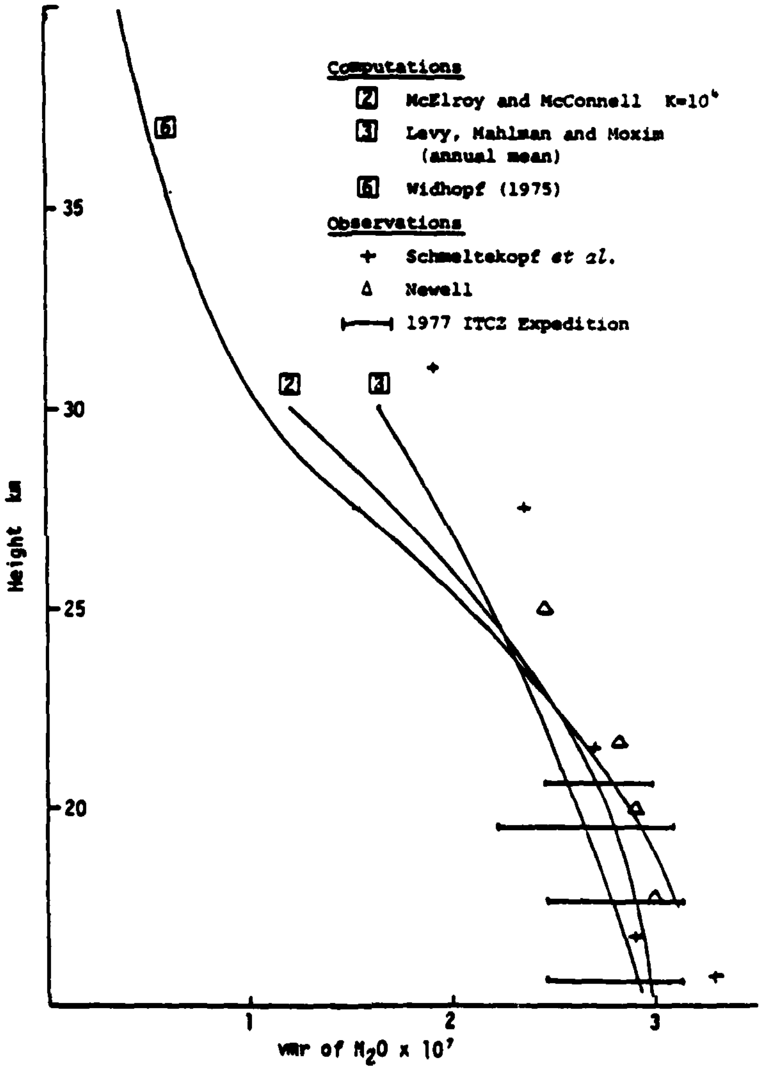


Fig. 3.19 Computations and observations of the concentration of N_2O, 10°N

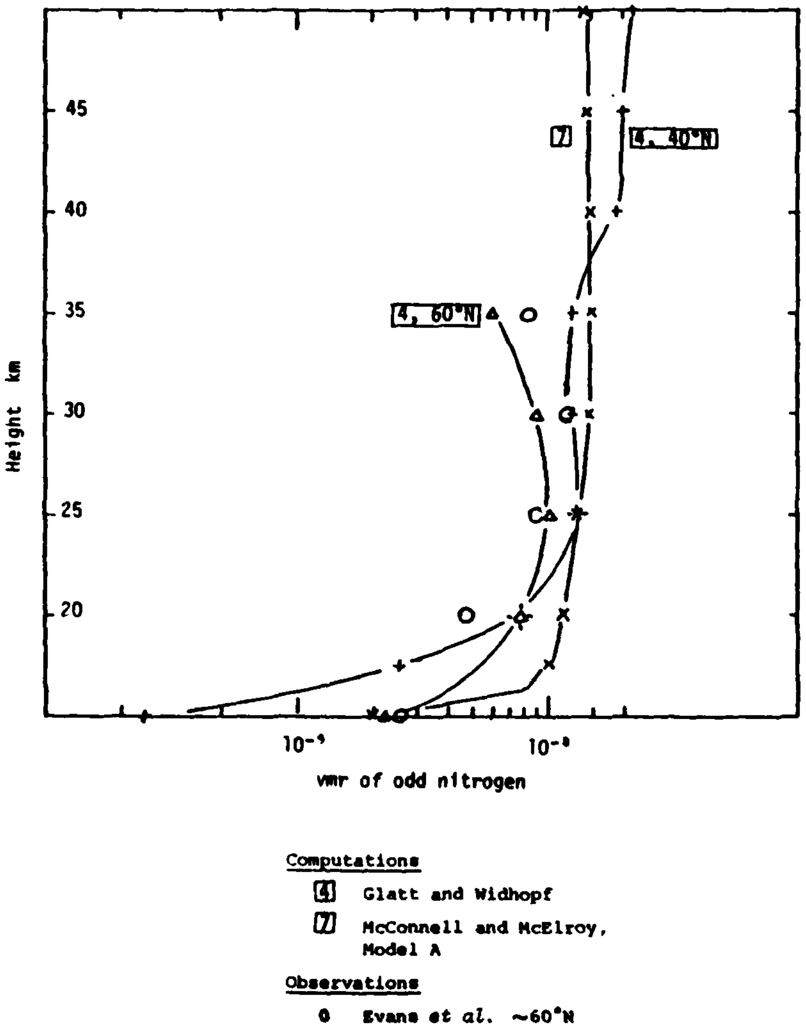


Fig. 3.20 Computations and observations of the concentration of total odd nitrogen

3.8 Implications of the transport hypothesis in study of the aircraft pollution problem

Assessment of the impact of exhaust emissions from commercial aircraft has been based almost entirely on the predictions of one- and two-dimensional chemistry/transport models relying on averaged mean motion fields and arrays of eddy diffusion coefficients. These models require or permit direct exchange of matter between the point of emission and the photo-chemically active region of the stratosphere. The FAA 'high' estimate of total fuel consumption in world-wide commercial operations in 1990 is 1.74×10^{11} kg yr^{-1}, of which 8.1×10^{10} is expected to be consumed in the airspace between 30°N and 60°N and 10 km and 16 km altitude, i.e., the 'box' BCED of Fig. 3.3. The total estimated consumption above 16 km is only about 2×10^{8} kg yr^{-1}.

The mass transport hypothesis which has been examined in this report appears to provide a useful empirical device for investigation of trace substances, which is in general not inconsistent with observation. The observational basis of one feature of the hypothesis is that the H_2O mmrs show that direct transport upwards from the 'box' BCED does not occur: the low general level of mmr above the line is not consistent with significant upward transport by mean motion, and the absence of substantial fluctuation of mmr is not consistent with significant eddy transport.* The basis of the second feature of our hypothesis is that the low general mmr requires entry at the equatorial tropopause and that observed winds and the global energy budget show that this entry must be preceded by ascent in precipitating cloud. Our transport hypothesis, therefore, requires that most of the aircraft emission should have a long tropospheric lifetime including some period in precipitating cloud. The nitrogen oxides have an involved tropospheric chemistry, and are unlikely to survive the process: the H_2O emissions are a negligible perturbation of the tropospheric water budget.

---

* The most recent observations using the rapid-response OH fluorescence instrument show a higher variability than previous measurements - See Fig. 3.16 and paragraph 3.5.2.

If the transport hypothesis is a true description of atmospheric motion, a model useful in the aircraft emission problem must have two attributes. It must correctly simulate dynamical processes around the 16 km level which appear to exclude upward transport by diffusion-like processes on any scale, and it must correctly simulate tropospheric processes including dynamics, cloud formation, precipitation, and a formidably complex trace substance chemistry. The motion envisaged cannot be simulated by a one-dimensional model and is not simulated by any existing two-dimensional model. In principle, any type of motion which actually exists should be diagnosed by a three-dimensional primitive equation model of sufficient resolution with boundary conditions based on the existing climate. The difficulty is with the resolution, and with the spurious diffusion introduced by finite difference solution. This difficulty is compounded when modeling the aircraft perturbation problem, where a near-discontinuity in the source distribution can be modeled only by a very high resolution grid in the vertical, since stable computation requires a smearing of the source over several contiguous levels. Any three-dimensional model capable of diagnosing motion of the type required by the transport hypothesis must have high resolution in the vertical near the height of the equatorial tropopause and its poleward extensions, and perhaps also near all tropopauses. This is true, *a fortiori*, of two-dimensional or three-dimensional models required to predict the effects of composition perturbations near these atmospheric levels.

Because of both the location of the projected source and the computational complications, it is suggested that high priority be given to confirming or rejecting the transport hypothesis. This report points to three relevant areas of inquiry. The first area is the accumulation of measurements of trace substances at all latitudes around the 16 km level, with particular attention to N_2O because of the relative simplicity of the stratospheric destruction process. The second area concerns details of the odd nitrogen budget. The major discrepancy in comparison of mass budget estimates by the transport hypothesis and by other means occurs in the ratio of odd N production to N_2O destruction. This ratio does not depend on a recognized major uncertainty in the transport hypothesis - the actual magnitude, rather than the minimum magnitude, of the annual mass exchange. Resolution of the question calls for many more measurements of total odd nitrogen around the 16 km level. This question is of interest to the FAA problem aside from its bearing on the validity of the transport hypothesis. The fact that models which produce approximately the same concentration patterns of total odd nitrogen may differ considerably in estimates of the total mass produced in the atmosphere reduces confidence in the modeled responses to a perturbation of the production rate. The discrepancies of modeled total production appear to be accompanied by discrepancies in modeled partition of odd N between the species. This assessment is based on very few observations: clearly more are needed, but all experience with chemically active stratospheric trace species shows that establishment of reliable concentration statistics is a slow and very expensive task.

The third area of inquiry relevant to the transport hypothesis concerns the details of water vapour concentration and cloud near the tropical tropopause. Again, more observations of water content are needed, preferably by instruments with the precision of the Lyman-α fluorescence detector, but statistics of minimum temperature and cloud distribution could yield useful, if not definitive, estimates of H_2O concentration. A major requirement is to expand the inquiry to all longitudes, since there is clear evidence of systematic longitudinal differences in the nature of the equatorial tropopause.

SECTION 4.0: Some Aspects of Aircraft Wake Phenomena

4.1 Position at the termination of CIAP

This position is set out in the following extract from CIAP 3.

"Aircraft wakes involve both fluid dynamic processes and chemical-kinetic processes. The fluid dynamic properties of the wake determine the conditions under which the chemical reactions take place. The important fluid dynamic parameters are static temperature, flow-residence times, and the degree of dilution of the engine-exhaust species and reactant products by mixing with the atmosphere. The chemical reactions in the wake do not significantly influence the fluid dynamic properties, since the reactions involve trace species. The fluid dynamic properties of the wake can be established without simultaneous consideration of chemical reactions. With the fluid dynamic properties known, chemical-kinetic computations can be carried out in an uncoupled fashion.

The aircraft wake can be conveniently subdivided into three regimes: the jet, the vortex, and the dispersion regimes. These regimes correspond to the fluid-dynamic processes that control the structure and growth of the wake in the subsequent time interval. The important characteristics of these regimes are summarized in table 2.1.

In the jet regime, the engine effluents are initially confined to individual exhaust jets. At the end of the jet regime the jets merge and are entrained in the rolled-up vortex. The flow times are between 1 and 10 sec, the precise time being a function of aircraft span, velocity, weight, and altitude. At the end of the jet regime, the size of the merged jets is O(100 m), and the dilution ratio due to air entrainment is $O(10^{-2})$.

Temperatures in the jet regime are $O(10^3\ K)$, and highly reactive species (H, O, OH, HO_2, HCO) exist in quantities of the same order as NO_x. During their lifetimes of a few tens of milliseconds, these species control

TABLE 2.1. Aircraft Wake Regime Characteristics

Jet regime	Vortex regime	Wake-dispersion regime
• Fluid-dynamic characteristics - Flow times: t ≈ 1-10 sec - Symmetrical jet growth followed by jet merging - Size: 10-100 m - Dilution ratio: $0(10^{-2})$	• Fluid-dynamic characteristics - Flow times: t ≈ $10\text{-}10^{2}$ sec - Primary growth in vertical direction due to vortex sinking - Size: 100-300 m - Dilution ratio: $0(10^{-3})$	• Fluid-dynamic characteristics - Flow times: t ≈ $10^{2}\text{-}10^{3}$ sec - Dispersion mechanisms: • wind shear • wake and atmospheric turbulence • gravitational collapse • buoyant rise - Size: 0(1,000 m) - Dilution ratio: $0(10^{-4})$
• Chemical-kinetic characteristics - Flow temp.: $T > T_\infty$ - Reactive species: H, O, OH, HO_2, HCO - Important reactions: $NO_2 + OH\ (+M) \rightarrow HNO_3(+M)$ $NO + HO_2 \rightarrow NO_2 + OH$ $NO_2 + O \rightarrow NO + O_2$ $NO_2 + H \rightarrow NO + OH$ - Characteristic chemical time: $10^{-2}\text{-}10^{-1}$ sec	• Chemical-kinetic characteristics - Flow temp.: $T \approx T_\infty$ - $[HNO_3]_{jet} \approx [HNO_3]_{vortex}$ - No significant chemistry	• Chemical-kinetic characteristics - Flow temp.: $T \approx T_\infty$ - $[HNO_3]_{jet} \approx [HNO_3]_{dispersion}$ - Half time for NO_x/O_3 catalysis >> 10^{3} sec
• Conclusion - $NO_x \rightarrow HNO_3$ conversion ≤ ~ 10-20%	• Conclusion - No significant chemistry	• Conclusions - No significant chemistry - Ozone destruction in 10^{3} sec undetectable - Contrail critical temperatures 190-200 K

the chemistry. Some conversion of NO_2 to relatively inert HNO_3 by reaction with the abundant hydroxyl radicals (OH) takes place. Detailed plume chemical-kinetic calculations predict an upper-bound conversion of NO_x to HNO_x of only 10-20 percent.

In the vortex regime, the flow times are between 10 and 100 sec. The primary fluid-dynamic process is sinking of the vortex pair accompanied by mass detrainment. The result is a vertical spreading of exhaust effluents with little or no horizontal spreading. At the end of the vortex regime, typical wake dimensions are 100 to 300 m. The corresponding dilution ratios are $0(10^{-3})$. In this regime, no significant chemistry takes place. The flow temperature is approximately ambient, and the concentration of all reactive species has decayed to a level where the reaction times are greater than the flow time. As a consequence, the HNO_3/NO_x ratio is frozen.

In the dispersion regime, there is a transition of wake-growth mechanisms from aircraft-induced perturbations to atmospheric dispersion. In this regime, such wake-growth mechanisms as wake turbulence, gravitational collapse, and buoyant rise due to temperature excess gradually dimish. The flow times are between 100 and 1,000 sec. Typical dimensions and dilution ratios are 1,000 m and $0(10^{-4})$, respectively.

No chemical effects of any significance occur in the dispersion regime. All of the ambient atmospheric ozone chemistry is in operation, of course, but the halftimes for HNO_3 chemistry or catalytic destruction of ozone are very long compared to flow times. The ozone depletion due to the one-way $NO \rightarrow NO_2$ reaction, which establishes the correct steady-state NO_2/NO split, amounts only to about one percent after 10^3 sec.

The water-vapor concentrations in the wake correspond to saturation temperatures of approximately 190 to 200 K. If the ambient temperature is below these values, contrails will form."

4.2 Jet regime chemistry

Since the CIAP report was written, the rate constant of one of the 'important reactions' $NO+HO_2 \rightarrow NO_2+OH$ has been measured at atmospheric temperatures, and found to be greater by a factor of 30 to 40 than that assumed in the CIAP process, so that computed concentrations of the HO_x species would be expected to change considerably on use of the new value. There appears to be a case for recomputing the jet regime chemistry, but several considerations suggest delay.

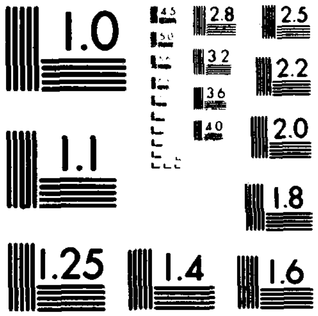
- The rate constants would be required over a wide range of temperature.

- The HO_x species concentrations appear to be very dependent on the existence and concentration of unburned hydrocarbons in the gas entering the jet regime. The ultimate degree of NO_x-HNO_3 conversion might be very dependent on precise operational details.

AD-A089 100   CENTER FOR THE ENVIRONMENT AND MAN INC HARTFORD CONN   F/G 4/1
THE PERTURBATION OF SOME ATMOSPHERIC MECHANISMS BY EMISSIONS FR--ETC(U)
NOV 79 G D ROBINSON   DOT-FA77WA-4055
UNCLASSIFIED   CEM-4232-667   FAA/EE-80-16   NL

2 of 2
AD
A089100

END
DATE
FILMED
10-80
DTIC



MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

- The uncertainty concerning the NO_x content of gas entering the jet regime (different methods of measurement produce different answers) does not yet appear to have been resolved.

- Current models of the unperturbed atmosphere do not handle the NO_x/HNO_3 ratio question particularly well.

- If the transport hypothesis put forward in Section 3 of this report is correct, the emissions of aircraft flying the 1990 projected pattern (99 percent below 16 km) would have a potential lifetime of months in tropospheric conditions before reaching chemically active regions of the stratosphere. The degree of immediate conversion from NO_x to HNO_3 is in this case of much less importance than for flight above 16 km as envisioned in CIAP.

When environmental problems of stratospheric operations of the magnitude contemplated in CIAP, with aircraft of specified performance, again arise, it would be prudent to reexamine the jet regime chemistry.

4.3 Contrail formation

There is no difficulty of principle in deciding whether or not, in specified circumstances, a condensation trail will form behind any aircraft. Ambient temperature and H_2O concentration must be known, together with the excess over ambient of the heat and water content of the exhaust. The treatment of the problem in CIAP 3 needs no amendment, but it centered on stratospheric flight with the ambient mass mixing ratio around $2\text{-}3 \times 10^{-6}$. For the 1990 traffic projection with 99 percent of the fuel consumption below 16 km, a reexamination of the contrail problem is required. Fig. 4.1 is a section of the standard Appleman (1957) diagram for heights between 10 and 16 km on which the 45°N January and July Standard Atmosphere temperatures are plotted. There is clearly a high probability of formation of ephemeral condensation trails. To investigate the probabilities of meso- and synoptic-scale events, (as for example by Barrett in CIAP 3,

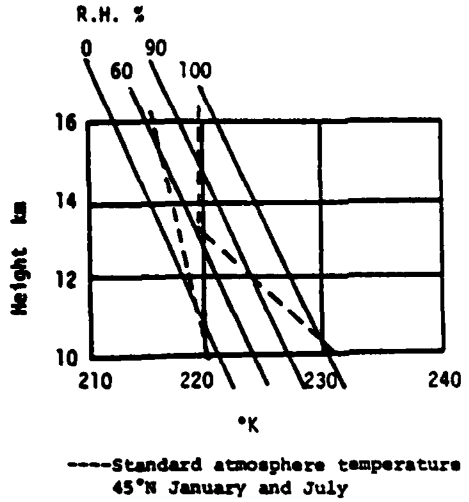


Fig. 4.1 Appleman contrail diagram. Condensation trails form if the ambient atmospheric temperature is to the left of the appropriate ambient humidity line. The trails may be non-persistent.

Chapter 7) would require joint statistics of ambient water vapour mixing ratio and temperature in the flight pattern. These statistics do not exist. Humidities measured by radiosonde are unreliable at heights of 10 km and above; practically the only reliable humidity measurements in the height range of interest were made on the occasions from which the Tables and frequency diagrams of Section 3 of this report are compiled.

Statistics of condensation trail formation are required to assess the possibility of resulting climatic effects, including the attenuation of solar radiation of all wavelengths. The minimum requirement is for area of sky covered as a function of height. Emissivity and attenuation coefficient for solar radiation are also required, but might be estimated from water content. However, when these factors are known, the appropriate perturbation of cloud structure must be entered into some atmospheric model. In this writer's opinion, such an approach would be unprofitable at present: uncertainties in specification of the normal (unperturbed) cloud structure are at least comparable with the likely perturbation, and the dynamics of possible effects of the perturbing high cloud on lower cloud layers are not incorporated in existing models.

Condensation trail formation does, however, appear to introduce the possibility of reduction of solar radiation (including erythemal U.V) at the ground by amounts of order one percent in some regions with very low natural lower cloud amounts, which is as large a climatic impact as any other now expected from the projected 1990 fleet. At present the form of investigation most likely to produce useful information would be a simple observing program, in flight as well as on the ground. Special observing instructions (and in flight some instrumentation) seem called for - past attempts to document condensation trail formation from standard high cloud observations have not had much success.

REFERENCES

Ackerman, M., D. Frimout and C. Muller, 1977: Stratospheric CH_4, $HC\ell$, and ClO and the chlorine-ozone cycle, Nature, 269, pp. 226-227.

Appleman, H. S., 1957: Derivation of jet aircraft contrail-formation curves. Tech. Report 105-145, Air Weather Service, Washington, DC.

Bannon, J. K., R. Frith and H. C. Shellard, 1952: Humidity of the upper troposphere and lower stratosphere over Southern England, Geophys. Mem., London Meteor. Office, No. 88, Vol. 11, 33 pp.

Bolin, B., 1979: On the role of the atmosphere in biogeochemical cycles, Quart. J. Roy. Meteor. Soc., 105, pp. 25-42.

Bradley, J. H. S., 1979: Realistic physics requires modern numerical methods, Fourth Conference on Numerical Weather Prediction. Preprint volume, pp. 209-212, Amer. Meteor. Soc., Boston, Mass.

Brewer, A. W., 1949: Evidence for a world circulation provided by the measurements of helium and water vapour distribution in the stratosphere, Quart. J. Roy. Meteor. Soc., 75, pp. 351-363.

Bush, Y. A., A. L. Schmeltekopf, F. C. Fehsenfeld, D. L. Albritton, J. R. McAfee, P. D. Goldan and E. F. Ferguson, 1978: Stratospheric measurements of methane at several latitudes, Geophys. Res. Letters, 5, pp. 1027-1029.

Cothern, C. R., 1979*: A preliminary analysis of N_2O including a materials balance, EPA-560/6-79-001.

Cluley, A. P. and M. J. Oliver, 1978: Aircraft measurements of humidity in the low stratosphere over Southern England, 1972-1976, Quart. J. Roy. Meteor. Soc., 104, pp. 511-526.

____________________, 1979: An observation of unusually high humidity in the lower stratosphere, Quart. J. Roy. Meteor. Soc., 105, pp. 306-309.

Danielsen, E. F., 1959: The laminar structure of the atmosphere and its relation to the concept of a tropopause, Archiv Meteor. Geophys. Bioklimat. All, pp. 293-332.

Donahue, T. M., 1977: Hydrogen. Studies in Geophysics - The Upper Atmosphere and Magnetosphere, N.A.S., Washington, DC, pp. 72-83.

Dütsch, H. U., 1978: Vertical distribution of ozone on a global scale, Pure Appl. Geophys., 116, pp. 511-529.

Ehhalt, D. H., L. E. Heidt, R. H. Lueb and N. Roper, 1974:* Vertical profiles of CH_4, H_2, CO, N_2O and CO_2 in the stratosphere. Proceedings, Third Conference on the Climatic Impact Assessment Program, DOT-TSC-OST 74-15, pp. 153-160.

Evans, W. J., and seven others, 1978: Stratospheric constituent measurements from project stratoprobe (Abstract), WMO Symposium on changes in the composition of the stratosphere, Toronto, June 1978, WMO publication 551, pp. 55-59.

Fraedrich, K., 1978: Structural and stochastic analysis of a zero-dimensional climate system, Quart. J. Roy. Met. Soc., 104, pp. 461-474.

_____________, 1979: Catastrophes and resilience of a zero-dimensional climate system with ice-albedo and greehouse feedback, Quart. J. Roy. Met. Soc., 105, pp. 147-168.

Glatt, L. and G. F. Widhopf, 1978: Aircraft HO_x and NO_x emission effects on stratospheric ozone and temperature, NASA Contractor Report 158945.

Harries, J. E., 1976: The distribution of water vapour in the stratosphere, Rev. Geophys. Space Phys., 14, pp. 565-575.

Harshvardhan, 1979: Perturbation of the zonal radiation balance by a stratospheric aerosol layer, J. Atmos. Sci., 36, pp. 1274-1285.

Helliwell, N. C., 1960: Airborne measurements of the latitudinal variation of frost-point temperature and wind, Meteor. Office Scientific Paper, No. 1, London HMSO, 30 pp.

_______________, and J. K. Mackenzie, 1957: Observation of humidity, temperature, and wind at Idris 23 May - 2 June 1956, Met. Res. Pap. No. 1024, Meteor. Office, London.

________________, J. K. Mackenzie and M. J. Kerley, 1957: Some further observations from aircraft of frost-point and temperature up to 50,000 ft., Quart. J., Roy. Met. Soc., 83, pp. 257.

Hidalgo, H., 1978: Status of representative two-dimensional models of the stratosphere and troposphere as of mid-1978, Report No. FAA-AEE-78-23. (I.D.A. paper P-1341)

Hilst, G. R., C. duP. Donaldson and R. Contilliano, 1973: Some analyses of the chemistry and diffusion of SST exhaust materials during Phase III of the wake period, ARAP Report 199, NASA CR-132323.

Hunten, D., 1975:* The philosophy of one-dimensional modeling, Proceedings, Fourth Conference on the Climatic Impact Assessment Program, DOT-TSC-OST-75-38, pp. 147-155.

Johnston, H. S., K. Kattenhorn and G. Whitten, 1976: Implications of carbon-14 data for the period 1963-1965 for models of stratospheric motion and the reduction of ozone by SST's, J. Geophys. Res., 81, pp. 368-380.

Kerley, M. J., 1960: Analysis of cloud distribution between London Airport and Johannesburg from Comet in-flight reports, Meteor. Mag., 89, pp. 297-300.

____________, 1961: High-altitude observations between the United Kingdom and Nairobi, Meteor. Mag., 90, pp. 3-18.

Kley, Dieter, E. J. Stone, W. R. Henderson, J. W. Drummond, W. J. Harrop, A. L. Schmeltekopf and T. L. Thompson, 1979: In situ measurements of mixing ratio of water vapor in the stratosphere. MS submitted for publication, J. Atmos. Sci.

Krey, P., R. Lagomarsino and L. Toonkel, 1977: Gaseous halogens in the atmosphere in 1975, J. Geophys. Res., 82, pp. 1753-1766.

Kruger, A. J. and R. Minzner, 1976: A mid-latitude ozone model for the 1976 U. S. standard atmosphere, J. Geophys. Res., 81, pp. 4477-4481.

Kuhn, P., E. Magaziner and L. P. Stearns, 1976: Stratospheric areal distribution of water vapor burden and the jet stream, Geophys. Res. Letters, 3, pp. 529-532.

London, J. and T. Sasamori, 1971: Radiative energy budget of the atmosphere, Space Research, 11, pp. 639-649.

Lorenz, E. N., 1967: The nature and theory of the general circulation of the atmosphere, World Meteorological Organization, 161 pp.

Levy, H.,II, J. D. Mahlman and W. J. Moxim, 1979: A preliminary report on the numerical simulation of the three-dimensional structure and variability of atmospheric N_2O, Geophys. Res. Letters, 6, pp. 155-158.

Mastenbrook, H. J., 1968: Water vapor distribution in the stratosphere and high troposphere, J. Atmos. Sci., 25, pp. 299-311.

__________, 1971: The variability of water vapor in the stratosphere, J. Atmos. Sci., 28, pp. 1495-1501.

__________, 1974: Water vapor measurements in the lower stratosphere, Can. J. Chem., 52, pp. 1527-1531.

Mahlman, J. D., 1975:* Some fundamental limitations of simplified-transport models as implied by results from a three-dimensional general-circulation/tracer model, Proceedings, Fourth Conference on the Climatic Impact Assessment Program. DOT-TSC-OST-75-38, pp. 132-146.

Manabe, S. and R. T. Wetherald, 1975: The effects of doubling the CO_2 concentration on the climate of a general circulation model, J. Atmos. Sci., 32, pp. 3-15.

Manley, G., 1953: The mean temperature of central England 1698-1952, Quart. J. Roy. Met. S., 79, pp. 242-261.

McConnell, J. C. and M. B. McElray, 1973: Odd nitrogen in the atmosphere, J. Atmos. Sci., 30, pp. 1465-1480.

McElroy, M. B. and J. C. McConnell, 1971: Nitrous oxide, a natural source of stratospheric NO, J. Atmos. Sci., 28, pp. 1095-1098.

Murgatroyd, R. J., P. Goldsmith and W. E. H. Hollings, 1955: Some recent measurements of humidity from aircraft up to heights of about 50,000 ft over Southern England, Quart. J., Roy. Meteor. Soc., 81, pp. 533-537.

NAS/NRC, 1976: Halocarbons - effects on stratospheric ozone, Washington, D.C., National Academy of Sciences, 352 pp.

NRC/NAS, 1978: Nitrates: an environmental assessment, Washington, DC, National Academy of Sciences, 723 pp.

Oliver, M. J. and A. P. Cluley, 1978: A systematic error in the measurement of frost-point using a Meteorological Office MK3 hygrometer, Quart. J. Roy. Met. Soc., 104, pp. 503-509.

Oliver, R. C., E. Bauer and W. Wasylkiwskyi, 1978: Recent developments in the estimation of potential effects of high altitude aircraft emissions on ozone and climate, Report No. FAA-AEE-78-24 (I.D.A. paper P-1343)

Ramanathan, V. and R. E. Dickinson, 1979: The role of stratospheric ozone in the zonal and seasonal radiative energy balance of the earth-troposphere system, J. Atmos. Sci., 36, pp. 1084-1104.

Reiter, E. R., E. Bauer and S. C. Coroniti (Eds.), 1975:* The Natural Stratosphere of 1974 - CIAP Monograph 1, Washington, DC, U.S. Department of Transportation, DOT-TST-75-51, 1192 pp.

Roach, W. T., 1962: Aircraft observations in the lower sub-arctic stratosphere in winter, MRCP121, Meteor. Office, London, 13 pp.

____________, 1967: On the nature of the summit areas of severe storms in Oklahoma, Quart. J. Roy Met. Soc., 93, pp. 318-336.

Robinson, Elmer and R. C. Robbins, 1975: Gaseous atmospheric pollutants from urban and natural sources, "The Changing Global Environment," pp. 111-124, S. Fred Singer, Ed., Dordrecht/Boston, D. Reidel.

Robinson, G. D., 1964: Surface measurements of solar and terrestrial radiation during the IGY and IGC, Annals of the IGY, Vol. 32 - Meteorology, pp. 17-61.

______________, 1978: Water vapor in the lower stratosphere (Abstract) EOS, 59, p. 1085.

______________, 1978: Weather and climate forecasting as problems in hydrodynamics, Mon. Weather Rev., 106, pp. 448-457.

Robinson, G. D., H. Hidalgo and R. Greenstone, Eds., 1975:* The stratosphere perturbed by propulsion effluents, CIAP Monograph 3, Washington, DC, U.S. Department of Transportation, DOT-TST-75-53, 718 pp.

Schmeltekopf, A. L., D. L. Albritton, P. J. Crutzen, P. D. Goldan, W. J. Harrop, W. R. Henderson, J. R. McAfee, M. McFarland, H. I. Schiff, T. L. Thompson, D. J. Hofmann and N. T. Kjome, 1977: Stratospheric nitrous oxide altitude profiles at various latitudes, J. Atmos. Sci., 34, pp. 729-736.

Schneider, S. H. and R. E. Dickinson, 1974: Climate Modeling, Rev. Geophys. Space. Phys., 12, pp. 447-493.

Singh, H. B., L. J. Salas, H. Shigeishi and E. Scribner, 1979: Atmospheric halocarbons, hydrocarbons and sulfur hexafluoride, Sci, 203, pp. 899-903.

Sutera, A., 1980: On stochastic perturbation and long-time climate behaviour, submitted for publication Quart. J. Roy. Met. Soc.

Tucker, G. B., 1975: An analysis of humidity measurements in the upper troposphere and lower stratosphere over Southern England, MRP1052, Meteor. Office, London, 35 pp.

Widhopf, G. F., 1975:* A two-dimensional photochemical model of the stratosphere, including initial results of inert tracer studies, Proceedings, Fourth Conference on the Climatic Impact Assessment Program, DOT-TSC-OST-75-38, pp. 316-331.

____________, and L. Glatt, 1979: Two-dimensional description of the natural atmosphere including active water-vapour modeling and potential perturbations due to NO_x and HO_x aircraft emissions, Report No. FAA-EE-79-07.

---

* These documents are available from the National Technical Information Service (NTIS), Springfield, VA 22161 USA.

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-311-586/253