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several possible sources. Diurnal observations of N and NO concentrations and more measurements of O and O_2 seasonal variations are needed. Much work remains to be done on metallic ions and neutrals and sporadic E in the lower E region.

In future studies the lower ionosphere must be considered as a portion of a very complex system which is coupled to the lower atmosphere and the magnetosphere.

Minor Constituents in the Stratosphere and Mesosphere

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This paper is a brief survey of a portion of the research on trace constituents in the stratosphere and mesosphere between 1971 and 1974. A primary motivation for much of the stratospheric research came from the realization that man's activities may influence global climate and the atmospheric ozone content, our shield against certain UV wavelengths. A great deal of progress has been reported in understanding both the present background stratosphere and the responses to be expected from additions of nitrogen oxides, water, and chlorine oxides, especially with respect to ozone. Trace constituents in the mesosphere have been modeled and measured to increase our understanding of the physics and chemistry of the mesosphere but also to relate mesospheric composition and transport to ionospheric processes at higher altitudes, to D region ion chemistry, and to upper stratospheric composition.

Atmospheric constituents whose partial pressures or volume mixing ratios are less than 10^{-6} of the corresponding value of the ambient atmosphere are termed minor constituents. It is only in this way that the species discussed here may legitimately be termed minor because their importance far outweighs their numbers in most respects. Life itself directly depends on O_3, CO_2, and H_2O. The earth's climate is largely controlled by CO_2, H_2O, and O_3, because like many minor constituents they interact strongly with electromagnetic radiation, especially the infrared. Certain of these species are sensitive indicators of important physical and chemical phenomena: they are tracers of atmospheric motions, indicators of man's activities and of changes in solar activity. Consequently, it is small wonder that 1971-1974 saw a great deal of research on minor constituents in the atmosphere. Rather, it shocks one to realize how little was known in 1970 [*SMIC*, 1971] and how much remains to be determined now. Here I try to review progress in stratospheric and mesospheric studies, but I leave such a survey of tropospheric work to others.

STRATOSPHERE

Much of the stratospheric research in 1971-1974 was motivated by the realization that man's activities can affect global climate, either by increasing the aerosol burden or decreasing the ozone content of the atmosphere or both. Attempts to estimate the size and direction of these effects (and others) require understanding of the natural atmosphere, and various relevant laboratory and atmospheric measurements were undertaken, as were theoretical and model studies. One

key issue was the extent to which fleets of stratospheric aircraft (SST's) might deplete the O_3 layer. In 1971, Johnston noted that these SST exhausts would contain enough nitrogen oxides (NO_x) to remove significant quantities of O_3 globally. Yet at the time, despite the importance of the question, the processes controlling stratospheric O_3 in nature were not clear. For example, it was not yet established that naturally occurring NO_x compounds act as the major sink for O_3 in the stratosphere (a widely held belief in 1974).

The suggestion that catalytic reactions involving NO_x, O_3, and O were important in nature's O_3 balance appears to have originated with *Crutzen* [1970]. By that time it was fairly clear that consideration of only the pure oxygen reactions (Chapman mechanism) and those involving hydrogen oxides (HO_x) could not explain observed O_3 abundances; too little O_3 was observed [e.g., *Crutzen*, 1971, and references therein]. By late 1974 it was widely accepted that natural NO_x controls stratospheric O_3 in the sense that consideration of the oxygen, HO_x, and NO_x system can explain O_3 measurements. This conclusion was based on measurements of atmospheric constituents, measurements and calculations of atmospheric transport rates, laboratory measurements of molecular properties and reaction rates, and mathematical modeling of atmospheric photochemistry and transport. As these subdisciplines grew and enriched each other, the overall arguments became more consistent.

Early model calculations of O_3 in this period were hampered by lack of data on NO_x constituents. With only sketchy figures at his disposal on total atmospheric NO, mesospheric NO, stratospheric HNO_3, and lower stratospheric N_2O, *Crutzen* [1971] proceeded to examine the O_3 balance with an

assumed value of background NO_x at the lower boundary of the model. He included two sources of stratospheric NO_x: (1) the reaction $N_2O + O(^1D) \rightarrow 2NO$ and (2) a downward flux from the mesosphere. He concluded from his calculated O_3 production and destruction rates and his N_2O and NO_x profiles that stratospheric O_3 could be modeled very well when NO_x (presumably from natural sources) were included.

Thus there was a great need for stratospheric measurements of NO_x and N_2O. As experiments progressed, they were aided by atmospheric models, but these experiments were also a source of guidance to future modeling efforts. After the detection and measurement of stratospheric N_2O by *Schutz et al.* [1970], data were reported by *Murcray et al.* [1972], *Harries and Stone* [1972], *Ehhalt* [1974], *Farmer et al.* [1974], *Ehhalt et al.* [1974], and *Harries et al.* [1974a, b]. These data generally agree; the volume mixing ratio f_{N_2O} is 0.25–0.3 ppm just above the tropopause, decreasing to about 0.1 ppm at 30 km with a further decrease above 30 km. Too few data are available to discern latitudinal variations. These N_2O altitude profiles have been used in model calculations of NO_x and O_3, as discussed below, but they have not been related to the ultimate source of N_2O at ground. In fact, *Hahn*'s [1974] conclusion that the seas represent a large net source of N_2O may imply that a major photochemical sink of N_2O is not yet identified. *Crutzen* [1974c] has also discussed this problem.

NO was measured in the stratosphere by *Ridley et al.* [1973, 1974], *Schiff* [1974a, b], and *Lowenstein et al.* [1974] by using chemiluminescent detection and by *Ackerman et al.* [1973, 1974], *Toth et al.* [1973], and *Fontanella et al.* [1974] by using infrared absorption of solar radiation, and by *Patel et al.* [1974] by using infrared absorption of laser light. These measurements are difficult to make quantitative [*Murcray et al.*, 1974b; *Schiff*, 1974b], especially those depending on absorption spectra at NO. Mixing ratios determined by infrared methods generally show higher values than those from chemiluminescent sensors [e.g., *Schiff*, 1974a], possibly due to overlapping absorption lines from other species. Data are available in these references from near-tropopause heights to about 40 km at many locations, seasons, and times of day.

NO_2 measurements in the stratosphere were reported by *Ackerman and Muller* [1972], *Harries and Stone* [1972], *Brewer et al.* [1973], *Ackerman et al.* [1974], *Murcray et al.* [1974a], *Harries et al.* [1974a], *Brewer et al.* [1974], and *Fontanella et al.* [1974]. The Brewer et al. studies measured the absorption of visible sunlight, while the other groups used infrared emission or absorption by NO_2. *Schiff* [1974a] and *Farmer* [1974] have intercompared many of the available NO_2 data. One can see only an order-of-magnitude kind of agreement in the measurements. Both Schiff and Farmer also discuss the key parameter, the NO_2 to NO ratio: the two species must be measured simultaneously, at least in ratio, to test current understanding of NO_x control of O_3 [*Crutzen*, 1970; *Johnston*, 1971]. Another feature of the NO_2 picture which requires further study is its diurnal behavior. *Brewer et al.* [1973, 1974] deduce noon maxima in NO_2 profiles, opposite to those predicted by the photochemical theory of stratospheric NO_x. *Johnston* [1974] has reexamined the Brewer et al. data and finds an alternative interpretation of their data, one with no midday maximum.

In the present understanding of NO_x in the stratosphere, HNO_3 is a passive reservoir of odd nitrogen molecules; HNO_3 mounts no attack on O_3. It is in this form that odd nitrogen is thought to leave the stratosphere toward eventual removal in the troposphere [e.g., *Nicolet*, 1974]. HNO_3 has been measured in the stratosphere by many, including *Murcray et al.* [1972,

1973, 1974a], *Lazrus et al.* [1972], *Lazrus and Gandrud* [1974], *Fontanella et al.* [1974], and *Harries et al.* [1974a, b]. Data to about 30 km show generally a few parts per billion, and the extensive data banks by *Murcray et al.* [1973] and *Lazrus and Gandrud* [1974] also indicate definite layers of enhanced HNO_3 concentrations, more HNO_3 toward the poles, and some seasonal variations.

Theoretical or model studies of stratospheric NO_x have been fruitful and numerous. Attention has focused on calculating O_3 in an oxygen-hydrogen-nitrogen atmosphere. A recent review by *Crutzen* [1974a] summarizes many relevant processes and contributions. Subject to several prominent uncertainties in molecular properties (discussed clearly by *McElroy et al.* [1974] and *McConnell and McElroy* [1973]) it has been possible to compute O_3 profiles that agree reasonably well with O_3 observations. One-dimensional model results for O_3, including SST perturbations, have been presented by *Crutzen* [1974a, b, c], *Wofsy and McElroy* [1974], *McElroy et al.* [1974], *Wofsy* [1974], and many others, and reviewed by *Chang and Johnston* [1974]. Multidimensional studies have been undertaken by *Hesstvedt* [1972, 1974], *London and Park* [1974], *Alyea et al.* [1974], and others. In the one-dimensional models, vertical transport is parameterized by an eddy diffusion coefficient K. Such a parameterization has been extremely useful in aeronomy [e.g., *Colegrove et al.*, 1965; *McElroy and Hunten*, 1969]. A method for estimating K values versus altitude was presented by *Nicolet* [1971]. *Wofsy and McElroy* [1973] used Nicolet's method to generate K profiles based on available CH_4 measurements in the stratosphere, and they discussed certain limitations of the analysis. *Hunten* [1975] has also produced K profiles and expanded our understanding of this subject, and *Johnston et al.* [1974] have generated K profiles based on carbon 14 tracer studies.

Other key ideas on stratospheric NO_x concern the effects of atmospheric bomb testing [*Foley and Ruderman*, 1973; *Johnston et al.*, 1973], nuclear war [*Hampson*, 1974], and supernova explosions [*Ruderman*, 1974]. The suggestion that oxidation of NH_3 could lead to a source of stratospheric NO_x [e.g., *Junge*, 1963] has been explored by *McConnell* [1973], *McConnell and McElroy* [1973], and *McElroy et al.* [1974], but measurements of small NH_3 concentrations above ground level appear to rule out a significant effect [*Kaplan*, 1973].

In 1974, *Molina and Rowland* [1974a] proposed that the stratospheric O_3 balance would be seriously threatened by continued usage of man-made chlorofluoromethanes. Removal of O_3 would result from catalytic cycles involving Cl and ClO formed by the photolysis of CF_2Cl_2 and $CFCl_3$. This proposal was quickly reexamined in progressively more detail by *Cicerone et al.* [1974], *Crutzen* [1974b], and *Wofsy et al.* [1975] and in a manuscript not yet published by R. Turco and R. Whitten. From these first few investigations the problem seems very serious: only stratospheric photolysis appears to be a significant sink for these compounds, and no chain-terminating chemical processes have been identified for the chlorine oxide (ClO_x) catalytic cycles. Previous discussions of the catalytic removal of O_3 by ClO_x [*Stolarski et al.*, 1973; *Stolarski and Cicerone*, 1974] had focused on the possibility of natural volcanic and solid fuel rocket emission sources of ClO_x to the stratosphere, but other studies tentatively dismissed volcanoes as an important source, although they recognized the potential role of ClO_x [*Crutzen*, 1974a; *Wofsy and McElroy*, 1974]. In formulating their proposal, Molina and Rowland noted that temporally increasing ground level concentrations of $CFCl_3$ had been demonstrated by others. Late in

1974, similar findings were reported for CF_2Cl_2, and both compounds were measured in the stratosphere in concentrations that imply no significant tropospheric sinks. Stratospheric measurements of Cl, ClO, and HCl concentrations are needed to test and to refine the theoretical view of ClO_x in the stratosphere. The only quantitative measurements to date by *Lazrus et al.* [1974] show HCl mixing ratios that increase with altitude between 15 and 27 km to values of about 0.5 ppb. A positive gradient with altitude in the lower stratosphere is predicted if man-made chlorocarbons are the principal source of stratospheric ClO_x. *Farmer* [1974] and *Farmer et al.* [1974] have reported (tentatively) detection of HCl around 15 km. *Delany et al.* [1974] have occasionally observed Cl^- and Br^- on stratospheric aerosols. (*Crutzen* [1974a] has noted that bromine oxides can also catalytically remove O_3.)

Although a number of uncertainties remain to be investigated, several aspects of the potential effects of ClO_x should be noted: ClO_x is about 5 times as efficient at O_3 removal as NO_x, molecule for molecule; the injection altitude for Cl atoms due to the chlorofluoromethane source is about 30 km, in the region of photochemical activity for O_3; and finally, the O_3 depletion once initiated would last for decades. By contrast, the O_3 depletion if caused by proposed SST fleets would have lasted only 3-5 years after the cessation of stratospheric aviation. Outstanding questions include the possibility of chain-terminating reactions not yet identified, a lower or middle stratospheric sink for chlorocarbons that would not release free Cl or ClO, and the possibility that a significant natural cycle of stratospheric ClO_x already exists. Such a cycle could result from naturally produced compounds which could bear chlorine into the stratosphere. *Lovelock* [1974] has detected CCl_4, $CHCl_3$, CH_3CCl_3, and other compounds, but evidence shows that the observed CCl_4 may be completely anthropogenic [*Rowland and Molina*, 1975; *Molina and Rowland*, 1974b]. CH_3Cl has been detected in rather large amounts at ground level (R. Rasmussen, preliminary personal communication, 1974). At this writing it appears that man-made compounds, like CF_2Cl_2, $CFCl_3$, and CCl_4 and other possibly natural chlorocarbons (e.g., CH_3Cl) produced at ground level, after upward mixing, serve as the main source of stratospheric ClO_x. The analogy with ground level N_2O as the principal source of stratospheric NO_x can be seen.

Major contributions of observational data on O_3 itself included summaries showing O_3 trends [*Komhyr et al.*, 1971; *Angell and Korshover*, 1973; *London and Kelley*, 1974; *Pittock*, 1974], global patterns [*Dutsch*, 1974], numerous vertical profiles from rocket observations [*Krueger*, 1973], and the backscattered ultraviolet satellite method [e.g., *Prabhakara et al.*, 1971; *Mateer et al.*, 1971]. The global increase of O_3 between 1963 and 1970 has reversed; since 1970, all U.S. stations and most world data show O_3 decreases [*Machta*, 1974].

Atmospheric concentrations of CO_2 continued to increase [*SCEP*, 1970; *SMIC*, 1971], probably due to man's combustion of fossil fuels. Theoretical studies of atmospheric CH_4, CO_2, and CO appear to show, however, that the principal global source of atmospheric CO is oxidation of natural CH_4 [*McConnell et al.*, 1971; *Wofsy et al.*, 1972]. Measurements of stratospheric CH_4 were extended by *Ehhalt et al.* [1972], *Ehhalt and Heidt* [1973], *Cumming and Lowe* [1973], *Ehhalt* [1974], and others to altitudes above 60 km, while stratospheric CO measurements included those by *Seiler and Warneck* [1972] and *Goldman et al.* [1973]. Further modeling of carbon-containing species in the stratosphere and mesosphere was performed by *Shimazaki and Cadle* [1973] and *Whitten et al.*

[1973]. Much of the progress in understanding these species can be traced to the pioneering tropospheric studies by Levy [e.g., *Levy*, 1971, 1973]. *Wofsy et al.* [1972] also noted that CH_4 oxidation can also serve as an appreciable source of stratospheric H_2O. *Mastenbrook* [1971, 1974] reported extensive measurements from conversion of frost point temperature data of the stratospheric H_2O mean mixing ratio of 2-3 ppm. Similar values were found by *Harries* [1973] using infrared emission methods; earlier estimates showed much more H_2O. *Stanford* [1974] has discussed the problem and provides corroboration for the 'dry stratosphere.' Further data showing 1-2 ppm H_2O at 28 km came from *Patel et al.* [1974]. Other aspects of the dry stratosphere have been discussed by *Ellsaesser* [1974].

The pressing need for stratospheric measurements of atomic oxygen concentrations is not yet relieved, but prospects are good. *Anderson* [1974] has presented preliminary data from in situ resonance fluorescence instrumentation. His O concentrations do not appear to conflict with predictions, and the instrument looks promising. His plans to apply the method to OH measurements are greatly welcomed by atmospheric scientists because no data now exist despite the importance of OH in the NO_x and ClO_x cycles. The role of hydrogen oxides in atmospheric chemistry is critical, although it is now believed that they do not directly control stratospheric O_3 (see, for example, a review by *Schiff and McConnell* [1973]).

Sulfur-containing aerosols in the stratosphere were observed and discussed by a number of workers, including *Lazrus et al.* [1971] and *Cadle* [1972]. Extensive data now exist on the chemical composition of the particles, on the structure of the aerosol layers, and on their temporal variability [e.g., *Kondratyev et al.*, 1974]. SO_2, whether natural or anthropogenic, is suspected to be a gaseous precursor of sulfate aerosols [e.g., *Friend et al.*, 1973; *Davis*, 1974; *Harrison and Larson*, 1974]. It has also been suggested [*Clyne*, 1974] that sulfur oxides may directly affect O_3, but this appears to be unlikely [*Crutzen*, 1974a; D. M. Stedman and R. J. Cicerone, unpublished manuscript, 1974].

MESOSPHERE

Minor constituent composition of the mesosphere has similarly challenged many investigators. Odd nitrogen species, principally NO, are produced in the lower thermosphere and mix into the mesophere, which is a region of chemical loss for odd nitrogen [*Strobel et al.*, 1970; *Norton and Barth*, 1970; *Strobel*, 1971a, b, 1972]. Much of this subject has been reviewed by *Nicolet* [1974]. NO measurements have been reported by a number of workers in 1971-1974, including *Meira* [1971], *Tisone* [1973], *Rusch* [1973], and indirectly inferred values by *Narcisi et al.* [1972]. Several uncertainties remain, both in theory and in interpretation of measurements: for example, certain molecular properties and rates of atmospheric transport. For instance, it is not clear if the thermosphere, through the mesosphere, serves as a significant source of odd nitrogen for the upper stratosphere [*Strobel et al.*, 1970; *Strobel*, 1971a, b].

Another key question [*Strobel*, 1971a; *Rusch*, 1973] concerns the branching ratios of several N production mechanisms: How much $N(^4S)$ and $N(^2D)$ are produced? Models of the neutral mesosphere were also developed by *Shimazaki and Laird* [1970], *Brasseur and Nicolet* [1973], *Hunt* [1973], and *Bowman and Thomas* [1974]. The D region ionization processes related to neutral constituent chemistry have

been reviewed by *Reid* [1971], *Sechrist* [1972], and *Thomas* [1974]. Possible perturbations to mesospheric NO induced by aerospace operations have been modeled by *Stolarski et al.* [1974] and *Whitten and Turco* [1974]. For the altitude region 40–60 km it appears that the only measurements available are those of *Pontano and Hale* [1970], who have since revised their NO values downward by 50%.

Atomic oxygen measurements in the mesosphere have been reported by several groups, most recently by *Scholz and Offerman* [1974] from rocket-borne mass spectrometers, by *Donahue* [1974a, b] down to 80 km, and by *Dickinson et al.* [1974]. The Donahue concentrations were inferred from green line emissions measured on Ogo 6, and Dickinson's concentrations were inferred from a rocket-borne resonance lamp detection of O. Mesospheric O_3 concentrations have been measured directly and indirectly (see, for example, *Hays and Roble* [1973] and the references therein). The O and O_3 have been modeled for the mesosphere by *Shimazaki and Laird* [1970], *Turco and Sechrist* [1972], *Hunt* [1973], *Bowman and Thomas* [1974], *Crutzen* [1974a], *Park and London* [1974], and others.

Hydrogen-containing species in the mesosphere are interesting for many reasons: for example, as indicators of the behavior of species like CH_4 and H_2O from ground level sources, and as suppliers of the exospheric escape flux of hydrogen. The basic physics and chemistry of H-containing species have been discussed by *Strobel* [1972], *Hunt* [1973],

Hunten and Strobel [1974], *Liu and Donahue* [1974a, b, c], and others. Notable progress included clarification of the role of vertical transport [*Hunten and Strobel*, 1974] and the relation between stratospheric odd hydrogen to the exospheric escape flux [*Liu and Donahue*, 1974c]. Principal measurements were provided by *Ehhalt* [1974] for H_2, by *Evans and Llewellyn* [1973] for H, by *Anderson* [1971a, b] for OH, and by researchers cited above for H_2O and CH_4. Three phenomena, observations of noctilucent clouds, hydrated ions, and a light scattering layer in the mesosphere, have motivated continued research on H_2O in the mesosphere (see, for example, *Chesworth and Hale* [1974] and *Thomas* [1974] and references therein).

To conclude, the author is aware that this review may not be historically accurate in details and that it gives heavy emphasis to chemical composition of the stratosphere and mesosphere and to the CIAP stratospheric research. Little attention has been paid here to the fruitful investigations of atmospheric dynamics, ion chemistry, the laboratory work on molecular properties and chemical reaction rates, on remote sensing, and on aerosols and metallic species. Hopefully, it is clear that the period 1971–1974 was a very active one, if mostly because of threats to our climate and well-being.