Instrumental Requirements for Global Atmospheric Chemistry

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The field of atmospheric chemistry is data-limited, primarily because of the challenge of measuring the key chemical constituents in the global environment. Several recent advances, however, in rugged, portable, remote-sensing, ground-based instrumentation and accurate, fast-response airborne instrumentation have provided powerful tools for the understanding of stratospheric ozone, particularly in polar regions. Current discoveries of the role of heterogeneous chemical processes point to the need for better techniques for characterization of stratospheric aerosols. In the troposphere, advances in in situ, sensitive methods for detecting reactive nitrogen compounds have demonstrated the role that these compounds have in controlling global oxidation processes, but better measurements of the reservoir species by which the long-ranged transport of pollutant-reactive nitrogen compounds is thought to occur are urgently needed. The role of hydrocarbons, particularly those of natural origin, in ozone formation in rural areas has focused attention on the requirement for better speciation of these ubiquitous compounds. Lastly, rigorous instrument intercomparison experiments have provided unbiased estimates of measurement capabilities.

FIELD MEASUREMENTS ARE AT THE CORE OF ATMOSPHERIC chemistry. They reveal new phenomena, for example, the time series of overhead-column O_3 that revealed the Antarctic ozone hole. They permit the elucidation of processes, for example, the uptake of acid-forming oxidants into raindrops. They allow the assessment of theory, for example, the simultaneous measurements of O_3, chlorine and nitrogen compounds, and water vapor that confirmed the theory that man-made chlorine compounds are the cause of the Antarctic ozone losses. Indeed, progress in the field of atmospheric chemistry has been paced predominantly by the availability of new observations; that is, the field is data-limited.

This situation arises because of the acute challenge of measuring highly reactive species (which is where the action is) in the global atmosphere (and thus at generally low concentrations), and from a variety of platforms (vans, aircraft, and balloons). At the center of this challenge are (i) the conception of new types of sensors that can detect previously unmeasured key chemical species and (ii) the development of these sensors into a fieldworthy instrument of defensible competence. This gestation is not short, nor is it cheap.

Accordingly, in this article, we focus on what appear to be the next needed types of chemical instrumentation, particularly those that lie just beyond the current state of the art. We discuss chemical sensors, first for the stratosphere and second for the troposphere. In both cases, we outline the science that is dictating the needs and cite some of the current and emerging techniques that address them. We also summarize the approach to instrument-intercomparison campaigns that have been fruitful in assessing measurement capabilities. We focus on instrumentation for investigating atmospheric processes (as opposed to the monitoring of trends) and on nonsatellite methods.

Stratospheric Chemistry and Measurement Needs

The central chemical feature in the stratosphere is the photochemical production and loss of O_3. But O_3 production is not just oxygen chemistry. If a calculation of the stratospheric O_3 content is performed with known solar radiation flux for a hypothetical stationary atmosphere of pure O_2 (diluted 1:4 by N_2), two anomalies are apparent. Too much O_3 is predicted (*1*) by a factor of 2 or 3, and it is distributed incorrectly: the highest overhead-column abundances are predicted in the tropics and the lowest at the poles, which is the reverse of what is observed (*2*). These two anomalies signify, respectively, the occurrence in the earth's atmosphere of H-N-Cl chemistry (*3, 4*) and the importance of global atmospheric transport of O_3 by wind systems. Much past, present, and future research is focused on understanding this interplay of photochemistry and meteorology. Fundamental to these advances are unequivocal measurements of the trace species. Such observations serve not only to test chemical mechanisms but also to serve as tracers of the circulation.

Fast homogeneous chain reactions. The central reactions controlling the photochemical production of O_3 are:

$$O_2 + h\nu \rightarrow O(^3P) + O(^3P),\ \lambda < 242\ \text{nm} \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2}$$

$$O_3 + h\nu \rightarrow O_2 + O(^3P) \tag{3}$$

$$O(^3P) + O_3 \rightarrow O_2 + O_2 \tag{4}$$

where M is a third body and $h\nu$ indicates the input of light energy of appropriate wavelengths, λ. Chain reactions, such as that carried by NO and NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{5}$$

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$$\underline{NO_2 + O(^3P) \rightarrow NO + O_2} \qquad (6)$$

$$\text{net: } O + O_3 \rightarrow O_2 + O_2 \qquad (7)$$

control the loss of odd oxygen, $O + O_3$. To test the photochemistry rigorously, the species on the production and loss sides of the O_3 rate-of-change equation must be measured simultaneously:

$$\frac{d[O_3]}{dt} = 2J[O_2] - 2\sum_X k_X[O][XO] \qquad (8)$$

where J is the photodissociation rate coefficient of O_2; X = H, OH, NO, or Cl; and k_X is the rate coefficient of XO with ground-state oxygen atoms. Thus, to test this equation, which applies to a homogeneous volume element small enough so that dynamically induced fluctuations can be excluded, the solar flux over the appropriate wavelength range and the number densities of $O(^3P)$, OH, HO_2, NO_2, and ClO must be measured simultaneously with temperature to low systematic and random errors (*5, 6*). Furthermore, as a consistency check on the individual pairs of chain reactions

$$X + O_3 \rightarrow XO + O_2 \qquad (9)$$

$$\underline{XO + O \rightarrow X + O_2} \quad \text{(RDS)} \qquad (10)$$

$$\text{net: } O + O_3 \rightarrow 2O_2 \qquad (11)$$

(RDS, rate determining step) measurements of the densities of NO, H, and Cl would be important as well. The combination of the time constants of the reaction chains to destroy odd oxygen, namely 30 to 40 hours or longer, the rate of change of solar zenith angle, and the tight error requirements make a rigorous test of Eq. 8 a demanding task—one that has not yet been accomplished. Indeed, although a great deal of effort has been put into measuring the loss terms in Eq. 8, commensurate effort has not been put into measuring the odd-oxygen production term. It clearly should be.

The O_3 balance in the middle and upper stratosphere, which is considered to be dominated by simpler (compared to heterogeneous) gas-phase chemistry, is not handled correctly in current numerical models, which yield up to 30% less O_3 than what is observed (*6, 7*). In order to improve the understanding of the central chain reactions that control that balance, simultaneous, accurate measurements over volumes of thousands of cubic meters are needed. In situ measurements with fast-response instruments on balloons or very high altitude unmanned aircraft seem to offer the only possible approach.

The production and loss of free radicals. The number densities of the free radicals X and XO that carry the chain reactions are affected on time scales longer than 30 to 40 hours, because the photochemical processes that produce them and the recombination processes that convert them into reservoir species are influenced by the advent of darkness or descent to higher pressures, or both.

Hydrogen and nitrogen free radicals are produced principally by reaction of excited O atoms, $O(^1D)$, with source molecules from the earth's surface (*3, 8*):

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (12)$$

$$O(^1D) + N_2O \rightarrow NO + NO \qquad (13)$$

The $O(^1D)$ atoms are produced by the photodissociation of O_3 at wavelengths below 320 nm. The concentrations of $O(^1D)$ atoms are calculated to be so low that direct measurement does not appear to be possible. However, the high reactivity of $O(^1D)$ does mean that knowledge of its vertical profile is crucial to the construction of model-derived distributions of reactive species, and measurements to constrain this profile are badly needed. The convolution of the sharp edge in the transmitted solar flux induced by the Hartley band of O_3 with the sharp edge in the quantum yield of $O(^1D)$ from O_3 photolysis has the potential to make the $O(^1D)$ vertical profile in the atmosphere significantly different from what is currently calculated. Simultaneous measurements of the $O(^1D)$ production and the actinic flux, over a wide altitude range (for example, 10 to 40 km), are required.

Measurements of the reservoir species, produced by recombination of chain-carrying free radicals, are important because they constrain the interaction of the H-N-Cl chain reactions. The reactions

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (14)$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (15)$$

are typical examples. For such species and for examining the relation between source molecules and the free radicals they provide, simultaneous, accurate (better than 10%), fast-response (1 to 10 Hz) measurements of both classes of molecules have proved to be a powerful tool, as exemplified by the NO_y/N_2O relation (*9*), where NO_y is the sum of the reactive nitrogen species ($NO_y = NO + NO_2 + HNO_3 + 2N_2O_5 + HO_2NO_2 + ClONO_2$). Such techniques, if extended to other families, such as hydrogen ($HO_y = OH + HO_2 + 2H_2O_2$) and chlorine ($Cl_y = Cl + ClO + 2Cl_2O_2 + ClONO_2 + HOCl$), could facilitate powerful tests of numerical simulations of stratospheric composition.

Perturbations of ozone photochemistry by heterogeneous reactions. Initial predictions of stratospheric O_3 loss arising from continued emissions of chlorofluorocarbons (CFCs) were based on homogeneous gas-phase photochemistry (such as that noted above). The predicted maximum losses were to be in the upper stratosphere and were 5 to 10% in the overhead O_3 column but concentrated at low and middle latitudes. These predictions were for a stratosphere containing about 8 parts per billion by volume (ppbv) of Cl, which is a condition that would not be reached until decades into the 21st century at 1980 CFC emission rates (*10*). It was therefore a major surprise when O_3 losses of 40 to 50% in the column (*11*), and exceeding 90% locally (*12*), were observed in the Antarctic lower stratosphere in late winter and spring. This discovery served as a salutary reminder that atmospheric chemistry is still an observationally driven science.

The current Cl content of the stratosphere is only about 3 ppbv. Recent research (*10, 13, 14*)—the ground-based and airborne polar O_3 missions and laboratory studies—makes it clear that the Antarctic O_3 loss is occurring from chlorine chemistry induced by heterogeneous transformation of HCl and $ClONO_2$ into reactive forms on the surface of polar stratospheric cloud (PSC) particles. Although the basic question of cause and effect has been answered, many important ones remain, particularly because stratospheric Cl levels will continue to increase for many years, despite international restrictions on CFC production. The predictions of the future evolution of high-latitude O_3 loss and the extent and pattern of its spread to low latitudes will depend upon the successful execution and analysis of further measurement campaigns.

The measurements required are of various species involved in the chemical mechanism (*15–18*) currently postulated to explain the ozone hole:

$$HCl + ClONO_2 \xrightarrow{PSC} Cl_2 + HNO_3 \qquad (16)$$

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (17)$$

$$2\,(Cl + O_3 \rightarrow ClO + O_2) \qquad (18)$$

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \text{ (RDS)} \qquad (19)$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2 \quad (20)$$

$$\underline{ClO_2 + M \rightarrow Cl + O_2 + M} \quad (21)$$

$$\text{net: } 2O_3 \rightarrow 3O_2 \quad (22)$$

The RDS, the recombination of ClO to its dimer (*19*), is proportional to $[ClO]^2$ and is independent of O_3. The above mechanism can only work in the almost complete absence of nitrogen oxides, because NO_2 competes for the ClO by way of Reaction 15. It is believed that this almost NO_2-free state is reached by gravitational sedimentation of PSC particles containing nitric acid (*13, 14*). An additional mechanism involves bromine:

$$ClO + BrO \rightarrow Cl + Br + O_2 \quad (23)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (24)$$

$$\underline{Br + O_3 \rightarrow BrO + O_2} \quad (25)$$

$$\text{net: } 2O_3 \rightarrow 3O_2 \quad (26)$$

Among the remaining questions connected with polar O_3 are the following:

1) What is the stoichiometry of the PSCs: are they pure nitric acid trihydrate (*15, 17, 20*), or a more variable HNO_3-H_2O mixture?

2) Does the transformation of HCl and $ClONO_2$ occur on both forms of PSCs, that is, on nitric acid trihydrate and water ice?

3) What is the detailed speciation of reactive Cl and odd N, particularly within the region of largest O_3 losses?

4) What is the detailed physicochemistry of denitrification (*14*) in the absence of intense dehydration? Denitrification has been observed in both vortices (*14*) and cannot be quantitatively explained by current theoretical calculations. This process is important, because if it can occur above frost point, the atmospheric volume potentially subject to the perturbed chemistry is greatly increased and limits O_3 loss in sunlit air parcels.

5) To what extent can the polar vortices be approximated as containment vessels or flow reactors (*13, 21*)? Only a limit for the chemical mechanism can be established at present, unless the vortex can be legitimately viewed as a well-stirred fixed mass of air. If there is significant air flow through it or if there is significant longitudinal asymmetry, then accurate measurement of the distribution of species within the vortex and examination of the exchange of air across the vortex edge and through its base are vital. The questions of the transmission of polar O_3 loss to lower latitudes and of the possible expansion of the ozone hole are intimately connected with this issue.

The measurement requirements over and above current capabilities (*13, 14*) arising from these questions are:

1) Measurement of the chemical composition of stratospheric aerosol, including PSCs, as a function of particle size and temperature.

2) In situ, fast-response measurements of HCl, $ClONO_2$, and HNO_3.

3) Simultaneous, fast-response speciation of reactive Cl, N, and H. For budgetary purposes, such measurements need to be accompanied by measurements of the source molecules: N_2O for NO_y and total Cl, possibly separated into organic and inorganic components, for Cl_y. Simultaneous measurement of H_2O, CH_4, and H_2 is needed to complement any HO_y measurements.

4) Fast-response measurements of $CFCl_3$, CF_2Cl_2, and CHF_2Cl, when ratioed to N_2O, have the potential to allow an understanding of the extent of sinking motion in polar regions and of the movement of vortex air to lower latitudes. Characterization of these processes may in turn be vital for understanding both the residence time of CFCs and the O_3 depletion potentials of their replacements.

5) The overall collection of meteorological data needs to be improved in polar regions (for example, more radiosonde launches) to yield better defined input to circulation models.

The above list may appear somewhat daunting, but it is probably not beyond current and near-term future capabilities.

The importance of platforms in stratospheric measurements. It is not possible to make much headway in discussing the area of nonsatellite stratospheric instruments without considering the platforms upon which they are subject to be deployed. Before the discovery of the Antarctic ozone hole, attention was mainly focused on the photochemistry of the upper stratosphere, where theory predicted that the risk of O_3 perturbations was the greatest. The only platform capable of reaching these altitudes (~35 to 50 km) was the large balloon. Although many pioneering measurements of the 40 or more molecules involved in stratospheric photochemistry have been made in this way (*22*), there are severe limitations. Launch sites are very limited: a handful worldwide, mostly at mid-latitudes. Severe restrictions arising from wind speed both at the ground and aloft have made balloons of limited utility beyond the initial measurements. The ability to cover latitude and longitude is essential if the horizontal structure in species distributions is to be characterized and understood, and this requirement places a premium on deployability of platforms. In addition, contamination can make in situ balloon measurements problematical in phases of flight other than descent.

The discovery of the ozone hole, and somewhat controversial suggestions that its effects are being conveyed to mid-latitudes, have moved the focus from the upper to the lower stratosphere (below 25 km). Some of the central phenomena are just within reach of the ER-2 high-altitude aircraft, which is a version of the Lockheed U-2, as has been demonstrated by the airborne polar ozone missions (*13, 14*). These missions, which were made possible by earlier funding on a long-term basis to investigate stratosphere-troposphere exchange, demonstrated the power of precise (a few percent or better), fast (about 1 Hz), and simultaneous measurement of several quantities. Absolute accuracies (combining both random and systematic error) were generally better than 10 to 15%. In addition to the in situ instrumentation, a large observatory aircraft, a modified DC-8 airliner, carried lidar and spectroscopic instruments (*19–21*) looking upward from just above the tropopause (10 to 12 km). Currently, such lidar measurements are limited to O_3 and aerosol, and the spectroscopic techniques can determine only column abundance in absorption, by use of the sun or the full moon as source. But the body of data is impressively self-consistent, and there is a clear need to associate the high-resolution aircraft data with appropriate and better meteorological analysis.

Ozonesonde measurements from Antarctica, performed every few days throughout the year from small balloons, have proved to be important (*12, 25*). A rich return could be made if measurements of water vapor and molecules such as CH_4, N_2O, and the CFCs could also be made by lightweight instruments on small balloons.

Ground-based observations of the stratosphere. Chemical change in the upper stratosphere, caused by changing emissions of the source molecules at the surface, has a long time scale because it takes decades to cycle the 95% or more of the atmosphere that lies below the altitudes of ultraviolet light penetration through the region above them. This prediction immediately places a premium on extended time series of regular, accurate measurements of stratospheric molecules that must have a well-understood, repeatable, and maintainable calibration. Such requirements are best met by ground-based instruments. Recent progress has included the evolution, after much effort, of Dobson spectrophotometer measurements of column O_3 abundance to the point where they are adequate to allow detection of significant changes in the composition of the Northern Hemisphere stratosphere and to allow the calibration of satellite systems (*10*). The discovery of the ozone hole was made with such an instrument that had been meticulously calibrated and because the data record had been subject to continual critical analysis (*11*).

The measurement of the column abundances of O_3 and O_3-related species by ground-based methods has also played a critical role in understanding the ozone hole. Absorption of ultraviolet and visible radiation has provided seasonal data on O_3, NO_2, OClO, and BrO levels (*24*). Aerosol lidars have also been operated from the ground with some success. From high or dry sites it has been possible to detect some stratospheric species, notably O_3, HNO_3, HCl, and HO_2, with the use of infrared or microwave methods having high spectral resolution (*25*). However, it has been difficult to obtain profile data when the atmosphere is viewed from below the number-density maxima and through a high-pressure, water vapor–laden troposphere. Siting some of the ground-based instruments at latitudes of about 65° is important for resolving whether O_3 loss occurs at the edge of the vortices.

Future developments in measurements of the stratosphere. Many nonsatellite stratospheric measurements have been made with spectroscopic methods at wavelengths from ultraviolet to microwave. These methods provide a generally unambiguous signature of molecular identity. However, the retrieval of mixing ratios by use of radiative transfer calculations becomes more difficult and the spatial resolution degrades as the optical path length over which the absorption or emission spectra are taken increases. In most spectroscopic measurements in absorption, the sun has been used as a source, and scanning through the atmospheric limb of the planet has frequently been used to gain sensitivity. The vertical resolution is in the range of 2 to 4 km; the information is averaged over hundreds of kilometers horizontally. Although profiles of many stratospheric molecules were measured in this way for the first time, it will be difficult for this approach to provide the power that has been so evident in the high-spatial-resolution measurements from in situ experiments in the lower stratosphere. Tunable diode lasers have developed to the point where they can be used as sources for absorption spectroscopy of some molecules. Instruments with these lasers can obtain measurements over spatial scales small enough (<10 km) that they are classifiable as in situ rather than remote-sensing instruments. This technique should be applicable to an increasing selection of molecules, particularly those having mixing ratios in the range of parts per billion by volume (ppbv) to parts per million by volume (ppmv). However, for reactive species such as OH, HO_2, BrO, and nitrogen oxides and atomic species in the vortex, where mixing ratios can be <1 part per trillion by volume, whatever technique can generate the requisite sensitivity on a case-by-case basis will probably be the way favored (*13*).

Better chemical and physical characterization of aerosols and PSC particles are clearly needed, as well as instruments that can be used to analyze better the various particle sizes. Laser-induced ionization mass spectrometry holds considerable promise for the study of aerosol and PSC particles.

Because fast-response, simultaneous measurements over large horizontal as well as vertical flight profiles are now required, all future state-of-the-art instruments will be designed for both stability of calibration and deployability. Unmanned aircraft may soon offer a way to obtain measurements over large areas; hence, lightweight and compact design are also desirable instrumental features.

There will continue to be a role for lidars (*13*), which have the potential to provide a "curtain" of data above and below a large manned aircraft. Measurements of temperature and pressure over the range of the lidars are needed in order to convert number density to mixing ratios. Analyses of a greater variety of species, including some of the more abundant molecules such as water vapor, N_2O, methane, and so forth, would also be highly desirable. Other high-quality, ground-based observations in the long term (*26*) have essential monitoring roles to play, possibly complemented by small balloon measurements of O_3, water, and some source molecules.

The availability of high-altitude, long-endurance unmanned aircraft is an exciting prospect for stratospheric chemistry in particular and lower stratosphere–upper troposphere research generally. The Boeing Condor (*27*), for example, can fly for a few days continuously, carry payloads of ~900 kg, and reach a ceiling of ~21 km. Design initiatives for flexible, unmanned aircraft that can be optimized for a particular choice of ceiling, payload, and endurance are being actively pursued (*28*). The advantages of such unmanned aircraft with an in situ payload include deployability in otherwise inaccessible regions, ease of recovery, rapid and flexible turnaround of instruments and data, and widespread accurate and precise sampling in a region where other techniques are not at their best. Importantly, instruments can be calibrated at will, and many internal consistency checks are provided in a multi-instrument payload. Such an effort is necessary if we are to understand and thereby predict the mechanisms of O_3 depletion in the lower stratosphere.

Tropospheric Chemistry and Measurement Needs

The chemistry of the earth's lower atmosphere is the set of processes by which compounds released near the earth's surface are oxidized to compounds that are either chemically inert, such as CO_2, or that can be removed from the atmosphere by wet or dry deposition, such as for nitric acid. Hence, oxidation is the lower atmosphere's principal cleansing mechanism, and O_3 plays a key role. Measurement of many of the chemical species that are participants in the oxidation processes occurring in the global (that is, nonurban or nonregional) atmosphere places acute challenges on instrumentation.

The role of ozone in tropospheric oxidation. The central role of O_3 arises because its photolysis by solar ultraviolet radiation

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{27}$$

initiates almost all tropospheric oxidation. Namely, the subsequent reaction of the excited $O(^1D)$ atom with water vapor forms the hydroxyl radical, OH, which is involved with most of the oxidizing transformations. In these reactions, OH is converted to the hydroperoxyl radical, HO_2, which reacts with compounds such as O_3 or NO to reform OH. This process is illustrated for the reactions that are thought to be responsible for the oxidation of CO

$$OH + CO \rightarrow H + CO_2 \tag{28}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{29}$$

where the course of subsequent reactions depends on the abundance of nitrogen oxides. When nitrogen oxides are elevated, the process is

$$HO_2 + NO \rightarrow OH + NO_2 \tag{30}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{31}$$

$$\underline{O + O_2 + M \rightarrow O_3 + M} \tag{32}$$

$$\text{net: } CO + 2O_2 \rightarrow CO_2 + O_3 \tag{33}$$

Whereas, when $NO_x = NO + NO_2$ species are at low levels, Reactions 32 and 33 become

$$\underline{HO_2 + O_3 \rightarrow OH + 2O_2} \tag{34}$$

$$\text{net: } CO + O_3 \rightarrow CO_2 + 2O_2 \tag{35}$$

Thus, OH and HO_2 drive the catalytic cycle that controls CO oxidation. But, with sufficient nitrogen oxides present, Reactions 30 to 33, the conversion of NO to NO_2 with HO_2 (Reaction 30), followed by the photolysis of NO_2 (Reaction 31), yield a second set of catalytic reactions that are responsible for the formation of O_3. With low nitrogen oxides, Reactions 30, 31, 34, and 35 occur, and O_3 is destroyed. Similar catalytic reaction sequences have been postulated for the oxidation of methane and the nonmethane hydrocarbons (NMHC).

To date, the understanding of these central reactions has been derived solely from laboratory studies and computer modeling of the chemistry. Neither the concentration of OH nor that of HO_2 have been measured in the atmosphere with instruments of sufficient reliability to demonstrate whether the current mechanistic understanding of these fundamental processes is adequate. The requirements for such instruments are challenging. Although huge quantities of OH are generated during the sunlit hours by the photolysis of O_3, the great reactivity of these oxidizing radicals implies that their atmospheric concentrations are small, typically 10^7 cm^{-3} or less (*29*). Moreover, these free radicals can be lost by collision with instrumental surfaces, that is, inside sampling inlets. Hence, although substantial effort has already been invested in the development of methods to measure OH, definitive measurements in the troposphere are still to be done (*29–31*). Techniques that are currently under development include in situ methods, such as laser-induced fluorescence (*32*) and a radioactive tracer technique (*33*), and long-path methods, such as laser absorption (*34*).

The role of ozone in global climate change. Because of its role in shaping tropospheric photochemistry, O_3 plays an important role in global climate change by influencing the concentrations of globally distributed, chemically active, greenhouse gases such as methane. In addition, O_3 itself is a radiatively important trace species (that is, a greenhouse gas) and, like CO_2, the concentration of O_3 in the troposphere can influence climate. Thus, it is important on the basis of global change to understand the factors that control the distribution of O_3 throughout the world.

There are two principal sources of tropospheric O_3. Some of the O_3 in the troposphere is from subsidence of O_3 from the stratosphere (*35*). In addition, the concentration of O_3 in the troposphere is changed by the oxidation processes outlined above, which produce O_3 when there is sufficient NO_x but destroy O_3 when there is not (*36–38*).

Throughout most of the troposphere, the production of O_3 is limited by the concentration of NO_x (*37, 39*). Because NO_x has a short lifetime in the lower troposphere [from less than a day to a few days, depending on season and levels of NO_x and NMHC (*37, 39*)], the O_3 production potential is largely limited to regions near NO_x sources. With the present state of knowledge concerning the distribution of NO_x in the atmosphere and the factors that shape this distribution, the magnitude and even the sign of the net O_3 production throughout most of the troposphere is uncertain.

Only recently have techniques become available that can measure global NO_x (*40–44*). These methods include laser-induced fluorescence (LIF) (*45*) and chemiluminescence (*46*) for NO, and LIF and chemiluminescence-photolysis (*47*) for NO_2. In addition, long-path NO_2 photo-absorption techniques, which have laser-light sources coupled with diode-array spectrometry (*31, 48*), are being developed.

Limited measurements with these techniques have been carried out in the remote free troposphere (*49, 50*). These observations indicate that the concentration of NO_x is surprisingly large; mid-latitude free-tropospheric mixing ratios (*49, 51*) are 30 pptv. These NO_x levels are sufficient to allow the free troposphere to become a region of net O_3 production. However, the sources of this NO_x are not well quantified. The natural sources of NO_x in the remote free troposphere are lightning and subsidence of NO_x from the stratosphere, and the principal man-made source in these regions is emissions from mid-latitude air travel in the Northern Hemisphere. An alternative possibility is that longer lived reactive NO_y compounds, such as HNO_3 and peroxyactyl nitrate (PAN), are transported from continental NO_x source areas to the remote troposphere, where these compounds are converted back to the chemically active NO_x forms.

Limited measurements of HNO_3 in the remote troposphere suggest that it is the dominant reactive nitrogen species, accounting for approximately 45% of the observed NO_y (*49, 52*). The photochemical decomposition of HNO_3 is calculated to be several weeks. This lifetime would allow HNO_3 to be transported over large distances. However, the limiting removal processes for HNO_3 in the remote upper troposphere is probably heterogeneous removal by aerosols or cloud water. Measurements are inadequate to allow assessment of the relative importance of these processes and to determine whether the removal is irreversible. Thus, it is not possible to set meaningful limits on the atmospheric lifetime of HNO_3, other than to note that the limited observations of the ratio of NO_x to HNO_3 appears to be much larger than would be predicted from photochemistry alone.

A key uncertainty with regard to these observations is measurements of nitric acid. The status of current capabilities to measure nitric acid was the focus of a ground-based intercomparison (*53*) that featured six methods: filter pack, denuder difference, annular denuder, transition flow reactor, tunable diode laser, and Fourier-transform infrared spectrometer. The reported nitric acid concentrations varied among methods by more than a factor of 2. The tests indicated that some of the sampling methods had artifacts or interferences associated with the sampling components (for example, the inlet or lines) or the operating procedures or detector specificity, or that alteration of the physical or chemical makeup of the ambient air occurred during sampling, such as shifts in the gas- and solid-aqueous-phase equilibrium of nitric acid, ammonia, and ammonium nitrates. Likewise, a more recent airborne intercomparison (*54*) involving three different measurement techniques—filter pack, tungstic oxide denuder, and tunable diode laser—indicated that there was substantial disagreement among these techniques at mixing ratios well above their respective detection limits. These difficulties limit the understanding of the role of long-range nitric acid transport in NO_x formation in remote areas.

Clearly, the measurement of nitric acid in the gas phase would provide valuable data for understanding the processes responsible for its formation and destruction. Also in this connection, the measurement of the concentration and chemical composition of nitrate in aerosols is needed. Besides nitric acid, many other important photochemical compounds can be incorporated and chemically processed in and transported by particles. As the results of the stratospheric studies have demonstrated, chemistry that does not occur through homogeneous gas-phase chemistry can occur readily by heterogeneous processes. In addition, these particles may play an even more significant role in global climate change than gas-phase compounds because of their impact on the earth's albedo. However, the technology is not yet available to analyze rapidly and precisely the chemical composition and size distribution of these particles in the atmosphere. Until the technology is improved, the lack of data on heterogeneous chemistry in the troposphere will remain a significant barrier to understanding.

Another source of NO_x in the remote free troposphere may be organic nitrates. This family of compounds, the most familiar of which is PAN, is formed by photochemistry in regions where the concentrations of NMHC are substantial (*55*). The organic nitrates have reasonably long lifetimes in the free troposphere and can be transported over substantial distances. However, they tend to be thermally unstable and can be photolyzed or can react photochemically to yield NO_x. Techniques capable of measuring the trace concentrations of PAN, as well as other organic compounds that are found in the remote troposphere, have been developed in recent years. The most common method is gas chromatography with electron-capture detection (*54, 56, 57*) and mass-spectrometric identification (*58*).

Measurements in the remote free troposphere have demonstrated that the level of PAN is not sufficient to account for the NO_x observed. However, a recently developed technique to measure NO_y, which uses catalytic reduction of NO_y compounds to NO followed by chemiluminescence detection (*41, 59*), has shown that only approximately 75% of the reactive nitrogen oxides could be accounted for as NO_x, PAN, HNO_3, and particulate nitrate (*57*). The remaining 25% was not identified but may be other organic nitrates. Assessment of whether sufficient NO_x could form from this unidentified nitrate component will require the identification of these other compounds, which represents a significant measurement challenge.

Finally, our understanding of the distribution of NO_x throughout the troposphere is based on a limited set of data. The methods for making more measurements are available, however. The drone aircraft mentioned above, the Boeing Condor, is capable of a continuous unattended flight of a few days in the remote free troposphere. A single flight by this aircraft carrying state-of-the-art NO_x measuring instruments could greatly expand the present data base concerning the distribution of NO_x in the remote free troposphere and its role in global O_3 formation.

The role of ozone as a pollutant. Tropospheric O_3 plays a third important role in the atmosphere: it is an important secondary pollutant that is harmful to plants, animals, and humans. Elevated and harmful levels of O_3 are being found in many urban areas of the United States and Western Europe during summer. Limited data suggest that harmful O_3 levels are also occurring in urban and industrial areas in Eastern Europe, Asia, and South and Central America. Moreover, daily maximum O_3 levels measured in rural areas of the United States are often comparable to those found in urban areas, and daily average levels can exceed urban levels.

Because of the high chemical reactivity and relatively large sources, NO_x and NMHC are thought to represent the most important O_3 precursors in most areas in the United States. This O_3 production can be represented by the simplified scheme

$$\mathrm{NMHC + OH + O_2 \rightarrow RO_2} \quad (36)$$

$$\mathrm{RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB} \quad (37)$$

$$\mathrm{HO_2 + NO \rightarrow NO_2 + OH} \quad (38)$$

$$\underline{\mathrm{2(NO_2} + h\nu + \mathrm{O_2 \rightarrow NO + O_3)}} \quad (39)$$

$$\text{net: } \mathrm{NMHC + 4O_2} + h\nu \rightarrow \mathrm{2O_3 + CARB} \quad (40)$$

where RO_2 is an organic peroxy radical and CARB denotes carbonyl compounds (aldehydes and ketones). In addition, the carbonyl compounds may undergo further photochemical reactions that will result in a net gain of hydrogen radicals and, in turn, produce more O_3.

The current O_3 abatement strategy is aimed at controlling anthropogenic NMHC. Long-term measurements with sufficient accuracy to detect relatively small systematic changes in NMHC atmospheric concentrations are required to determine whether this strategy is working. However, because of experimental difficulties and limited support, the NMHC precursors for O_3 have not been monitored with sufficient accuracy and precision. As a consequence, it is not known if the lack of success of O_3 abatement regulations is a result of a failure to achieve the targeted reduction in O_3 precursors or a flawed strategy. Furthermore, there is substantial debate concerning the relative importance of anthropogenic compounds versus natural compounds in the production of O_3. This issue revolves around several key chemical questions: (i) Is the O_3 produced regionally or locally? (ii) Does NO_x or NMHC limit the production of O_3? (iii) What is the role of the oxidation products of NO_x and NMHC in the formation of O_3? The data needed to address these questions are the atmospheric distributions of NO_x, NMHC, and their oxidation products.

Although there have been substantial advances during the past 10 years in NO_x measurement methods, the techniques to measure NMHC and their oxidation products are not adequate for the present scientific needs. The problems of analysis of the NMHC are complicated by the extreme complexity of the hydrocarbon mixtures that can be present in the atmosphere. More than 850 different hydrocarbons have been detected in gasoline vapor, and more than 300 different hydrocarbons have been labeled from vehicle exhaust. Natural hydrocarbons emitted by vegetation, which are currently estimated to account for approximate 50% of the NMHC emitted into the atmosphere in the United States, are mainly highly reactive olefinic compounds. However, over one-third of the natural compounds that are emitted are as yet unidentified. Air samples obviously can contain a great number of different hydrocarbons of natural and anthropogenic origin, and the oxidation of each of these species creates a mixture containing many additional oxidation products as well. It is clear that the analysis of the NMHC and their oxidation products is a formidable task.

The standard method for measurement of volatile organic compounds is by sample collection, followed by gas-chromatographic analysis with flame-ionization detection (FID). Because FID is nonspecific, a more specific detection scheme, usually mass spectrometry, is used to identify compounds. This process means that the measurement of hydrocarbons in the atmosphere is laborious and time-consuming: the accrual of adequate data bases to address regional air quality questions is thus quite difficult.

More importantly, however, the observations may be subject to major inaccuracies. Most of the current problems associated with volatile organic compounds analysis are associated with the trapping procedures. Large amounts of compounds, particularly high-carbon-number compounds, can be retained by the trapping medium. In addition, the presence of relatively large concentrations of oxidants in the sampled air may lead to further oxidation of the volatile organic compounds during the sampling process. The problems are particularly severe for NMHC at low concentration (<1 ppbv) and for heavier hydrocarbons ($>C_5$). Finally, at present, there are no proven techniques available to measure the partially oxidized volatile organic compounds.

Instrument Assessment by Intercomparison Experiments

It is a truism that a reliable estimate of the uncertainty in a measurement is as important as the measurement itself. With such an estimate, (i) observations and theory can be compared meaningfully, (ii) the results from separate campaigns can be merged reliably into a global data base, (iii) spatial gradients from separate data sets can be characterized credibly, and (iv) time series from different networks can be used to establish long-term records. During the past several years, the atmospheric chemistry community has devised a way to address instrument reliability in an arduous, but effective way: a formal and rigorous intercomparison of techniques and instruments.

The features of the most successful (that is, the most instructive) of those instrument intercomparisons have been the following: (i) involve several different techniques for measuring the same species; (ii) measure at the same place and time and under typical operating conditions, insofar as possible; (iii) state the accuracy and precision estimates in advance of the campaign; (iv) spike the atmospheric samples with privately known amounts of species that are potential artifacts; (v) prepare each investigator's results independently and separately (that is, blind) from the others and in a publication-ready status; (vi) compile jointly (or by an independent party) the separate results and assess the state of agreement or disagreement; (vii) publish the results and conclusions in a refereed journal; and (viii) repeat the process occasionally.

There have been several recent field campaigns devoted explicitly to the assessment of instrument reliability, as opposed to solely obtaining data to answer a geophysical question. Some of the campaigns have been carried out in a fashion close to the above ideal. A few of the conclusions were that (i) current techniques could not measure OH reliably at expected clean tropospheric concentration (*60*); (ii) methods are available to measure NO reliably even in remote (clean) regions (*42*); and (iii) the commonly used method for measurement of NO_2 is subject to substantial problems (factors of 2 to 3) with artifacts (sensitivity to non-NO_2 species) (*44, 61*). Furthermore, campaigns have also addressed how well numerous species can be measured with common platforms, such as balloons (*62*). Most of the intercomparison field campaigns, particularly those done fairly rigorously, have been rather humbling experiences.

Clearly, there remains much to be done and learned about instrument reliability. A pacing element is the availability of different techniques that address the same species with instruments that have completed separate field trials. Even with that necessary condition, the road to harmony can be long and twisting. For example, there is no one recipe for what to do when two or more methods disagree significantly.

Because both individual instrument development and tracking down the will-of-the-wisp discrepancies are arduous, time-consuming, and costly tasks, it should continue to be recognized that (i) multiple techniques are essential (and are not wasteful duplication) and that (ii) intercomparisons are vital (and are indeed as much a part of doing atmospheric science as is gathering data to test a geophysical hypothesis). The need is as simple as being able to demonstrate unequivocally that what we measure is indeed correct.

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