Analytical Techniques for Atmospheric Measurement

Edited by

Dwayne E. Heard
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Preface

In almost all of the scientific journals where data from field measurements are presented, it is the results, and how they have advanced our understanding of our complex workings of the atmosphere, that have received the most attention. We must not forget, however, that the instruments making the measurements are themselves state-of-the-art and highly specialised, having been first developed in the laboratory by chemists, physicists or engineers, before being applied to the measurement of atmospheric composition. There is usually insufficient space in the journal articles for a thorough description of the instrument, and often only essential details are given. Although there are a number of journals that specialise in the description of instruments, for example *Review of Scientific Instruments*, there is no common theme to a given issue, and an instrument to measure an important atmospheric constituent will likely be sandwiched between articles covering instruments from unrelated fields. Published proceedings from conferences or symposia devoted to instrumentation do offer some coherence, but the articles tend to be specialised, and although appealing to the highly expert reader, they are, in the main, not accessible to scientists wishing to further their knowledge in a new area. There are a number of textbooks that contain sections on instruments for measurements of atmospheric composition, but these usually do not cover recent developments, nor do they give a broad or detailed coverage of the techniques involved.

New analytical techniques or detectors are often invented by researchers with little or no interest in atmospheric science and are then ‘discovered’ by the atmospheric field measurement community, who go on to utilise the method to make significant breakthroughs. More recently, there has been a stronger collaboration between atmospheric chemists, physicists, engineers and analytical scientists, to develop bespoke instruments with the sole intention of measuring new species in the atmosphere. Sometimes a scientist in a core discipline, for example a physical chemist, recognises the need for a particular measurement in the atmosphere, and realises that the techniques they have used in the laboratory for fundamental studies can equally be applied in the field. Once a rarity, this practice is now becoming more common.

Aims of the book

The major aim of this book is to take the focus away from the results and the advances resulting from field measurements (very important though they are), and to place the emphasis on the instruments themselves: how they work, their strengths and weaknesses for a particular task, the platforms on which they have been deployed, how they are calibrated etc. The book explains the fundamental physical principles upon which the instrumental techniques are based. For instance, what properties of molecules can be exploited to enable their detection? What limits the sensitivity and accuracy of a given instrument, and what information can be gained from its use? Instruments developed to make measurements of atmospheric composition are highly specialised, but often have evolved over many years via several incarnations. The book attempts to convey the excitement of the challenge to *quantitatively* measure trace atmospheric constituents that are at the heart of atmospheric chemistry, and responsible for many of the problems facing society today; for example, the warming of our atmosphere, the destruction of the ozone hole, and the formation of urban air pollution and acid rain. Measurements of the composition of our atmosphere range from the earth's surface to the edge of space. Unsurprisingly, the most important species to measure, those that exert special control on our atmosphere, are often the most difficult to measure – only being present in miniscule concentrations as a result of being so reactive. For some species, for example the hydroxyl radical (OH), it has taken over twenty years of instrument development to enable a reliable and accurate measurement. In some cases, just a single measurement has opened up new areas for study – for example chlorofluorocarbon (CFC) measurements pioneered by Jim Lovelock using the electron capture detector.

Intended audience

The book is designed to appeal to two major types of audience. One class of readers are those who wish to gain a general understanding of instrumentation for measurement of atmospheric composition, the fundamental principles upon which techniques depend, their major capabilities, together with highlights of the important results and the advances in understanding that have resulted – but without wanting a detailed discussion of the underlying atmospheric chemistry or physics. The chapters have been written so that this information is easily retrievable, and is accessible to the non-expert. These readers will be final year undergraduates or postgraduate students starting out on a research project, or postdoctoral fellows or faculty (or indeed anyone) who wish to move into or learn more about composition measurements in the atmosphere. The other class of readers are field scientists or instrument developers who are more experienced, and who will be interested in the finer detail of specific instruments, and latest developments, and perhaps wish to discover if a particular technique were suitable for a new measurement. The individual chapters within this book contain a high level of instrumental detail not normally found in the literature due to lack of space in regular journal articles, and also include a discussion of the strengths and weaknesses of a particular method.

Intended outcomes

Upon completion of this book, it is hoped that you will be able to describe the analytical techniques that are used to make quantitative measurements in the atmosphere, and understand the physical principles upon which the techniques are based. You will be able to discuss, for each analytical method, issues such as species selectivity, calibration, sensitivity (lower detection limit), time-response, uncertainties (accuracy and precision), interferences and the method of data analysis. You will also be able to give examples of species that can be detected using the different techniques, with details of their detection, and describe the experimental platforms in the field on which instruments have been deployed, for example from the ground, ships, aircraft, balloons, rockets, satellites and spacecraft. You will be able to describe applications of the techniques used in the field to further understand the key chemical processes in the atmosphere facing our society today, and will be able to give specific highlights. Finally, it is hoped that you will be able to discuss why measurement of atmospheric composition in the field is such an important component of atmospheric science.

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Dwayne Heard
Leeds, November 2005

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Chapter 1

Field Measurements of Atmospheric Composition

Dwayne E. Heard

1.1 The role of field measurements in atmospheric science

1.1.1 Our changing atmosphere

It is difficult to switch on the radio or television, or open a newspaper, without being exposed to accounts of environmental concern resulting from a change in the composition of our atmosphere; for example, increased instances of drought or flooding as a result of the warming of our atmosphere through the increased emissions of greenhouse gases, or the increase in deaths attributable to a deterioration of urban air quality as a result of increased emissions of harmful gases and particles and their secondary oxidation products. Sensational documentaries based on the possible occurrence of some future apocalyptic event are becoming more widespread, and although in many cases they are not based on any scientific fact, the awareness of the general public on environmental issues is raised considerably. In a highly technological and information-rich age, it is becoming generally accepted that our atmosphere is changing as a result of mankind's activities, and if current trends are left unchecked, there may be dire consequences ahead. The key questions are, how quickly is our atmosphere changing and what can be done to mitigate the consequences? In order to predict the future changes in atmospheric composition, and hence the degree of expected climate change through global warming, numerical models are used extensively. The models require three types of input:

(1) An estimation of the future rates of emissions of trace gases. For natural emissions, for example isoprene from trees and plants, the rate of emission is strongly temperature dependent and hence there is a positive feedback with any future warming. For anthropogenic emissions, various scenarios for future use of fossil fuels are estimated, and many assumptions have to be made.
(2) The model must be able to disperse and mix trace gases away from emission sources, for example via advection by the wind or via convective uplift in weather fronts, and on a larger scale through global circulation.
(3) Following their emission, trace gases are removed from the atmosphere by solar-induced photolysis, chemical transformation or by physical deposition to surfaces, forming a large number of chemical intermediates and secondary species, which

themselves undergo further transformation. It is often the secondary products that are most harmful to the atmosphere, and it is crucial that the model contains an accurate description of the chemical mechanisms that describe the atmospheric degradation of trace gases emitted into the atmosphere.

1.1.2 The importance of atmospheric chemistry

The earth's atmosphere is oxidising not because of reaction of trace species with O_2 but owing to the presence of several key oxidising intermediates, which initiate the atmospheric removal of trace gases in the troposphere, eventually forming CO_2 and water vapour. The most important of these is the hydroxyl radical (OH), which is mostly generated in the daytime as a result of ozone photolysis to form electronically excited oxygen atoms, $O(^1D)$, which react rapidly with water vapour to form OH. The hydroxyl radical reacts with virtually all trace gases, including CO, hydrocarbons, oxygenated volatile organic compounds (VOCs), hydrochlorofluorocarbons (HCFCs), used as replacements for chlorofluorocarbons (CFCs) following their ban after the Montreal Protocol, and SO_2. Under normal circumstances, OH concentrations are very low at night, and the nitrate radical (NO_3) replaces OH as the major oxidising species. NO_3 is generated by the reaction of NO_2 with ozone, and reacts either by hydrogen atom abstraction or by addition to double bonds. Ozone itself is the third major oxidising species, reacting, for example, with unsaturated molecules through addition to double bonds forming ozonides which decompose to form a variety of unstable intermediates. Common to the oxidation by OH, NO_3 or O_3 is the formation of intermediate peroxy radicals, RO_2, where R is an organic fragment, including $R = H$, which reacts with nitric oxide, emitted following the burning of fossil fuels, to form nitrogen dioxide (NO_2). NO_2 gas is brown, as a result of strong absorption of sunlight in the blue and green parts of the spectrum, and is rapidly photolysed by sunlight ($\lambda < 400\,\text{nm}$) to form ground-state oxygen atoms, $O(^3P)$, which almost instantaneously combine with O_2 to form O_3, which is harmful to humans and plants in high concentrations.

The conversion of primary emissions, such as VOCs, eventually to CO_2 and water vapour can be extremely complex, involving several reactions. To give an example, *the Master Chemical Mechanism* (Jenkin *et al.*, 2003), http://mcm.leeds.ac.uk/MCM/, describes the complete oxidation pathways for the top 135 VOC emissions in the UK, and consists of 13 600 chemical species and 5900 chemical reactions. An important input to the model is the rate coefficient for each of these reactions over a range of conditions of temperature and pressure encountered in the atmosphere, and although many have been measured in the laboratory, the majority are not known and have to be estimated. In addition, solar-induced photodissociation and deposition to surfaces (the ground, ocean or aerosols) must be included to completely describe the chemistry of the atmosphere, and it is necessary in the laboratory to measure absorption cross-sections as a function of wavelength and temperature, and to measure photodissociation quantum yields as a function of wavelength, temperature *and* pressure.

The focus of this book is not about the chemistry in the atmosphere that is examined via field measurements, but the techniques by which the field measurements are made. The interested reader is referred to a number of excellent textbooks and review articles to discover more about the chemistry of the atmosphere, which in certain locations can be relatively simple involving a handful of species, but in polluted environments requires thousands of chemical species to adequately describe its complexities (Ehhalt, 1998; Finlayson-Pitts & Pitts, 2000; Ravishankara, 2003; Seinfeld & Pandis, 1998; Wayne, 2000). Suggestions for further reading are given in Section 1.11.

1.1.3 Why field measurements of atmospheric composition are important

The composition of the air we breathe was unknown until the second half of the eighteenth century, when carbon dioxide, nitrogen and oxygen were all discovered and isolated, with constituents at lower concentrations, such as methane and ozone, not being discovered until almost a century later. Since the first atmospheric measurements of ozone at ground level were made by Schönbein in 1858, scientists have continued to develop ever more sensitive instruments to discover and measure thousands of trace gases in the atmosphere. However, it is only in the last forty years or so that the link between concentrations of trace gases and global environmental issues has been made. Figure 1.1 shows the change in the mean global radiative forcings due to a number of agents in the period 1750–2000 (Houghton, 2005; IPCC, 2001). It can be seen that several trace gas species, and also

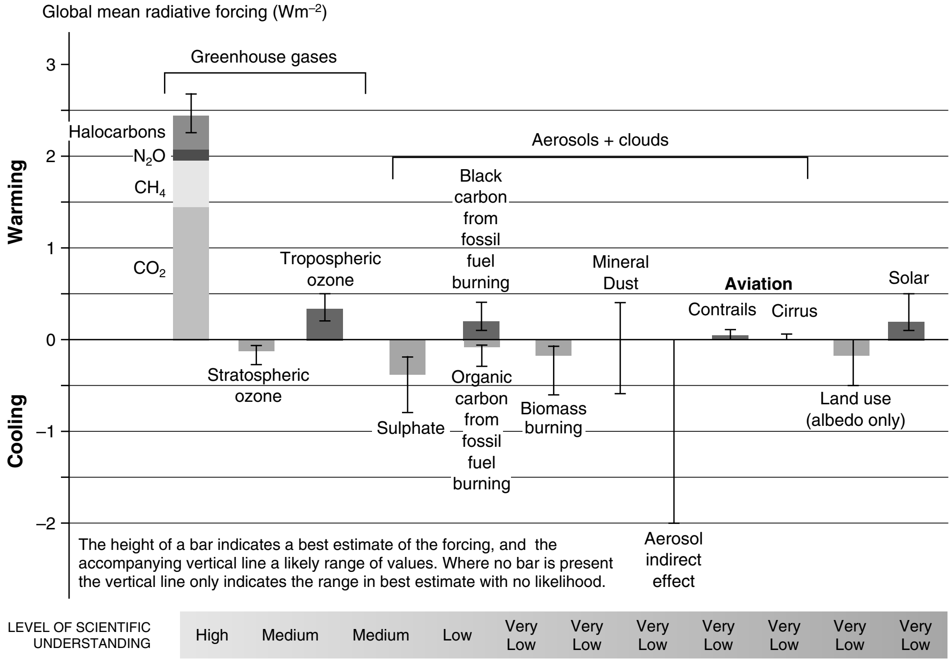


Figure 1.1 Anthropogenic and natural forcing of the climate for the year 2000, relative to 1750. Note that water vapour is also a greenhouse gas, but is not shown. Taken with permission from the 2001 report of the Intergovernmental Panel on Climate Control (Houghton, 2005; IPCC, 2001).

particulate matter (aerosols and clouds), are able to exert a global warming or cooling effect, or both. The graph is based upon our knowledge of the concentrations of these species, and how they interact with incoming or scattered solar radiation. Long-term and quantitative determination of these species in the atmosphere is crucial to calculate the individual contributions to global warming and hence climate change, and to inform policy makers. The concentration of greenhouse gases is increasing all the time, and their measurement is crucial to calculate future changes in atmospheric temperature (see Section 1.7.2). Understanding the trends in chemically and radiatively important gases and particles, and how they can be controlled in the future, is perhaps the most important challenge facing society today.

Field measurements are necessary over a wide range of temporal and spatial scales in order to record any long-term trends, and also to test how well models can predict the composition of the current atmosphere. Although a complete understanding of the complex process within our atmosphere requires an integration of field measurements, computer modelling and laboratory studies, almost all of the major breakthroughs have been initiated by field observations. Without the development of a suite of sensitive and accurate field instrumentation we would not be aware of the links between greenhouse gases/aerosols and global warming, the formation of ozone holes in the stratosphere, the deterioration in air quality on our cities, the changes in the oxidising capacity of the atmosphere, or other threats to our well-being.

An example is the discovery of the ozone hole, first observed in the mid-1980s as a reduction in the overhead column of ozone measured above Antarctica, measured from the ground using a Dobson spectrophotometer that relies on the absorption of ultraviolet (UV) light from the sun (UV absorption is covered in Chapter 3). These measurements were later confirmed using satellite measurements (see Section 1.4.8), with the ozone ‘hole’ demonstrating a marked spatial, altitudinal and seasonal dependence. An interesting aside is that the more sophisticated satellite instruments had recorded all the necessary data to observe the formation of the ozone hole, but the data analysis software had been programmed not to include data below a certain value! The ozone hole continued to grow in size and intensity, and the observations led to a flurry of activity amongst atmospheric chemists, who eventually postulated that heterogeneous chemistry occurring on the surface of polar stratospheric clouds that formed during the long Antarctic winter was able to generate active forms of chlorine that destroyed ozone when the sun returned. The work led to the Nobel Prize for Chemistry being awarded in 1995 to three scientists for their elucidation of the mechanism of formation of the ozone hole (but not to the instrument developers!). The postulated mechanism was proven beyond doubt by further field observations, as shown in Figure 1.2, that indicated a clear anti-correlation between concentrations of ozone and chlorine monoxide intermediates, measured by in situ instruments aboard the ER-2 research aircraft that flew into the stratospheric polar vortex from Patagonia.

Another example is the invention of the electron capture detector by Jim Lovelock, which enabled the detection of CFCs, present only at the part per trillion level (ppt, 1 part in 10^{15}), which led to the realisation that mankind was releasing into the atmosphere chemical species for which there were no natural removal mechanisms, and a species which if left unregulated could lead to disastrous consequences for stratospheric ozone. These field measurements of CFCs, followed by the understanding of the

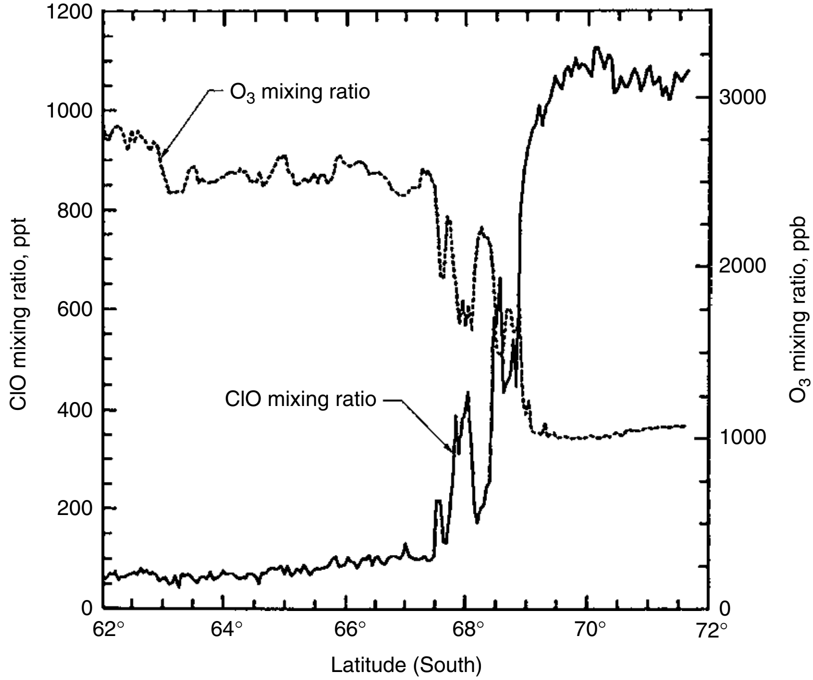
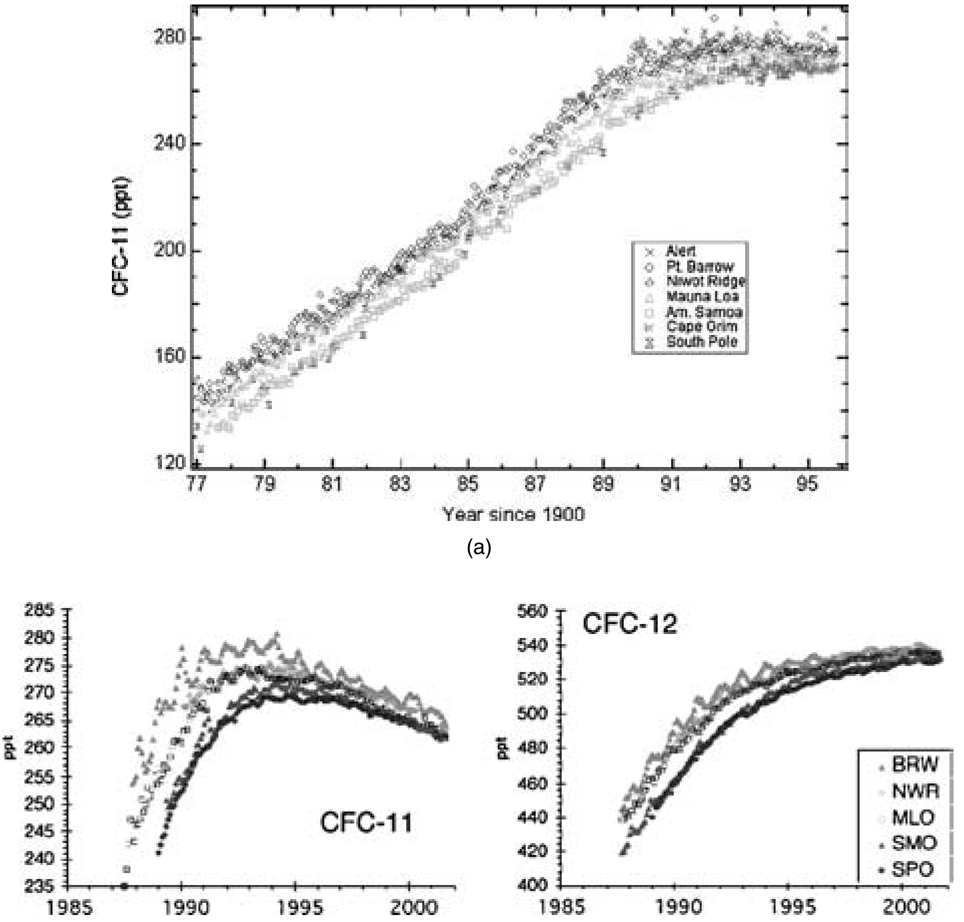


Figure 1.2 Concentrations of O_3 (UV absorption, Chapter 3) and ClO radicals (resonance fluorescence detection of Cl atoms following conversion of ClO by reaction with NO, Chapter 4) measured simultaneously aboard the NASA ER-2 aircraft as it flew into the polar vortex during a flight originating in Punta Arenas, Chile. There is almost perfect anticorrelation between rising ClO levels and the destruction of ozone. (Taken with permission from the American Geophysical Union, Anderson *et al.*, 1989.)

destructive nature of their degradation in the atmosphere, led to the implementation of the Montreal Protocol in 1987 and subsequent amendments. Concentrations of CFCs are now beginning to level-off, or are falling (dependent upon their atmospheric lifetime), as shown in Figure 1.3, but it will be at least several decades before critical chlorine loadings in the stratosphere fall below the threshold for formation of the Antarctic ozone hole.

During the heat wave experienced during the summer of 2003, when temperatures in the UK rose for the first time above 100°F (37.8°C), concentrations of ozone rose in the SE of England to 150 parts per billion (ppb, 1 part in 10^9), levels not observed for 20 years, yet at relatively low concentrations of nitrogen oxides (a result of stringent controls on exhaust pipe emissions). Field measurements of isoprene, a biogenic emission from plants, demonstrated concentrations that rose exponentially with temperature, with concentrations at the ppb level during the heat wave, sufficient to generate large quantities of ozone following its atmospheric oxidation. These measurements highlight the importance of including changes in the rate of biogenic emissions in any global climate change model.

Measurements by satellites have played a crucial role in understanding the effects of major volcanic eruptions. Stratospheric aerosols affect the atmospheric energy balance by scattering and absorbing solar and terrestrial radiation, and perturb stratospheric chemical cycles by catalysing heterogeneous reactions which markedly perturb nitrogen, chlorine



(a)

(b)

Figure 1.3 (a) Long-term trend (mixing ratios in pptv) of CFC -11 ($CFCl_3$) measured by ground-based instruments of the NOAA CMDL network since 1977. In the stratosphere the maximum is reached about 5 years later. (Data courtesy of Jim Butler and Jim Elkins, NOAA.) (b) More recent measurements of CFC-11 ($CFCl_3$) and CFC-12, from the same CMDL network. The atmospheric lifetimes of CFC-11 and CFC-12 are 45 and 100 years, respectively. The values for the northern hemisphere are slightly higher, because hemispherical mixing is always faster than the transport across the equator. The measurements are made using gas-chromatographs equipped with an electron capture detector. (Data courtesy of Jim Butler and Jim Elkins, NOAA.)

and ozone levels. These aerosols are small (0.1 μm radius) sulphuric acid solution droplets produced primarily through oxidation of sulphur dioxide injected into the stratosphere by volcanic eruptions. The Stratospheric Aerosol and Gas Experiment II (SAGE II) instrument, http://www-sage2.larc.nasa.gov/, launched on the Earth Radiation Budget Satellite (ERBS) in 1984, monitored the long-term global effects of the Mt. Pinatubo volcanic eruption in June–July 1991, which is estimated to have deposited 3.6×10^7 tonnes of aerosol material into the stratosphere. The instrument measured the stratospheric optical depth in the near-infrared ($\lambda = 1.02\,\mu\text{m}$). Measurements just after the eruption and again a year later showed that the volcanic material initially concentrated in the Tropics had spread across the entire globe. The Pinatubo aerosol layer warmed the local subtropical stratosphere by about 2.5–3℃ within three months of the eruption, and a statistically significant global average surface cooling was predicted by the end of 1992.

There is a need to continually develop new instruments to measure the spatial and temporal distributions of trace gases, be these harmful pollutants or short-lived intermediates, as these observations are required to monitor trends and as input to models and as target species to test the performance of computer models. There has been a phenomenal improvement in the measurement of many trace gases. Only 10 or 15 years ago, measurement accuracy for some trace species was limited to a factor of two, often with quite long averaging periods. An accuracy of 10% or less is now common, with averaging times in some cases of less than a second. New trace gases are being discovered all the time. The most powerful greenhouse gas ever discovered, SF_5CF_3, was measured by gas chromatography with detection via a magnetic sector mass spectrometer (see Chapter 5 for details) with mixing ratios of $\sim$0.005 pptv, trapped in air within snow in Antarctica (Sturges *et al.*, 2000). SF_5CF_3 is thought to be a by-product of the use of SF_6 by the electronics industry.

1.1.4 The challenges of field measurements in the atmosphere

Many field instruments have been developed to measure a very large number of trace species, whose mole fractions (or mixing ratios) in the atmosphere vary from the per cent level down to parts per quadrillion ($\text{ppqv} = 10^{-15}$). A crucial property of a trace gas is its atmospheric lifetime, which is defined as the time taken for the concentration to decay to $1/e$ (37%) of its initial value once its source is removed. The range of atmospheric lifetimes is truly enormous, varying from less than a second, as is the case for free-radicals such as the hydroxyl radical (OH) which mediates virtually all of atmospheric chemistry, to hundreds of years, for example CFCs. Figure 1.4 shows the atmospheric lifetime for a range of species together with the timescales for mixing processes across a range of spatial scales. The atmospheric lifetime determines the degree of transport away from the source region, and whether a trace gas is well mixed globally or exhibits significant spatial structure. The atmospheric lifetime of a trace gas is one of the most critical parameters when choosing the sampling strategy and detection method adopted for its measurement in the atmosphere. The atmospheric lifetime, τ, of a trace gas, X, is the reciprocal of the rate of removal, k', from the atmosphere, $\tau = 1/k'$ (Kurylo & Orkin, 2003; Ravishankara & Lovejoy, 1994). The rate of removal of X is the sum of the rates of photolysis (J, see Chapter 9), dry or wet deposition to surfaces and reactions in the gas phase. For some species photolytic removal or removal on surfaces can be dominant, but for the majority of trace species, k' is controlled by the rate of gas phase reactions, in particular with the hydroxyl radical, OH, and is given by:

$$k' = k_{\text{OH}+X}[\text{OH}] \tag{1.1}$$

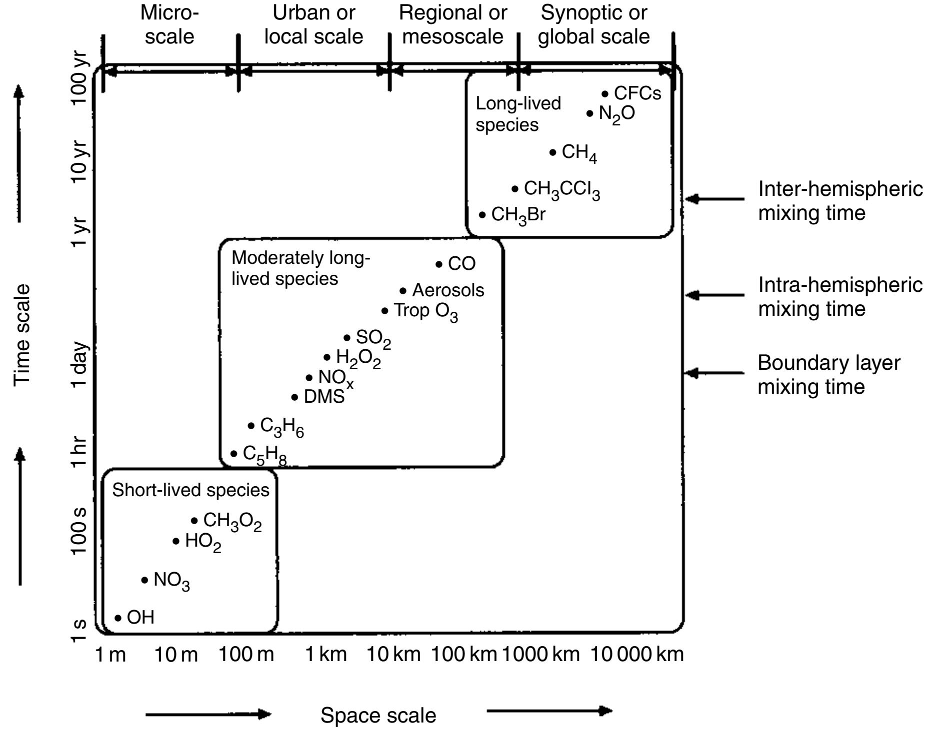


Figure 1.4 Lifetimes and distribution of atmospheric trace gases. The graph shows the very wide range of temporal and spatial scales over which atmospheric trace gases demonstrate variability in the atmosphere. (From Brasseur *et al.*, 1999, with credits to W.L. Chameides.)

where $k_{\mathrm{OH}+X}$ is the second-order rate constant for the reaction of OH with X and [OH] is the OH concentration. Thus it is critically important to know the concentration of OH, the quantitative measurement of which illustrates the serious challenges of field measurements. The importance of OH as the dominant oxidant in the atmosphere was recognised in the late 1960s/early 1970s, from which time a considerable effort worldwide has been invested in the development of field instruments for its detection. OH concentrations are very low, a typical daily maximum (at solar noon) being a few 10^6 molecule cm^{-3} ($\sim$0.1 pptv); OH reacts very quickly on surfaces, and will not be transmitted through sample lines; OH concentrations vary significantly on short spatial scales; OH lifetimes are very short ($\sim$1 s), and thus any measurement technique must be in situ, have excellent sensitivity, temporal and spatial resolution, and not be subject to interference from other species. For OH, in common with many other field determinations, it is this last criterion, namely the elimination of interferences, that is the most difficult to achieve. Laser-induced fluorescence (LIF) was suggested in 1972 as a suitable method for OH detection (see Chapter 4 for further details). However, while using this method an interference plagued OH measurements for many years, namely the laser photolysis of O_3 to generate $O(^1D)$, with subsequent reaction of $O(^1D)$ with atmospheric water vapour to generate OH. The first results in 1974 gave a maximum [OH] of 1.5×10^8

molecule cm^{-3}, with nighttime values of 5×10^6 molecule cm^{-3}, and at the time these were accepted, as model calculations of OH were subject to very large errors because kinetic data for key reactions relevant to OH were not accurately known. In the mid-1980s measurements by several instruments using LIF during the NASA GTE/CITE campaign were later discredited, with an evaluation panel concluding that OH concentrations had not been measured! The laser-generated interference is now well recognised, and current OH field instruments using LIF rely on a different excitation scheme and pressure regime, and are free from such interferences. Some thirty years or more after the first OH measurements, several methods are now routinely used to measure OH (Table 1.1), with reported accuracies as good as 10%. An important lesson was learnt by the entire community of the dangers of artefact signals, but this has led to the emergence of very rigorous acceptance criteria for new instruments to measure OH.

The concentration of trace species varies with latitude, longitude, altitude and time of day, sometimes on very short scales, and a wide range of instruments deployed on a variety of measurement platforms is required. The atmosphere displays a wide range of temperatures (from +50℃ (323 K) at the surface down to −130℃ (143 K) in the mesosphere), pressures (decreasing exponentially from 1 atm at sea level to 10^{-6} atm at 100 km above sea level), solar intensity and meteorological conditions (wind, snow, hail), and many practical and logistical barriers must be surmounted even to attempt a measurement.

1.1.5 Comparison with calculations from numerical models

Our understanding of atmospheric chemistry is manifested through atmospheric models which describe the main physical and chemical processes that control how trace gases and particulate matter are distributed spatially on local, regional and global scales, and also as a function of time. It is natural therefore to compare field measurements of atmospheric composition on a variety of temporal and spatial scales, using a plethora of instrumental techniques and platforms that are the subject of this book, with the calculations of numerical models. The field measurement alone of a trace species provides only limited information. Atmospheric models are used for a variety of purposes, for example to calculate future trends in greenhouse gases, such as methane, that control future changes in atmospheric temperature, or substances harmful to health, such as ozone, to define future air quality. Policy makers make extensive use of model predictions to define emission reduction legislation, which can cost the economy billions of pounds to implement. Whatever the application, the output of the desired model is only as good as the input (‘garbage in garbage out’), and as one of the model inputs is the chemical mechanism used to describe atmospheric transformation, it must be as accurate as possible.

Often the major degradation pathways are not known due to an absence of kinetic data on rate coefficients or product branching ratios, and these parameters have to be estimated using structure–activity relationships or numerical calculation (for which thermodynamic data are often required). In order to be confident about the ability of a model to calculate future atmospheric composition, it is important to design ways to test the accuracy of the mechanism used, and to identify which parts of it require

Table 1.1 Analytical techniques for selected classes of neutral atmospheric trace constituents

Class of constituent	Species	Analytical technique (chapter number)
Hydrogen compounds	OH	Laser-induced fluorescence (4), UV-visible DOAS (3), chemical ionisation mass spectrometry (5), far-IR emission spectroscopy (1)
	HO_2	Fluorescence (after conversion) (4), matrix isolation electron-spin resonance (1), peroxy radical chemical amplifer (7), far-IR emission spectroscopy (1), microwave absorption spectroscopy (1)
	H_2O vapour	Fluorescence after photolysis (4), IR absorption spectroscopy (2), surface acoustic wave (1), cavity ring-down spectroscopy (3), dew/frost point hygrometer (1), Lyman-α UV absorption (3)
	H_2O_2	IR absorption spectroscopy (2), liquid chromatography (after conversion, 8), chemiluminescence and fluorescence (after conversion, 7)
	H_2	Gas chromatography, reaction with hot HgO bed, Hg determined photometrically (8), mass spectrometry (5)
Nitrogen compounds	NO	IR absorption spectroscopy (2), UV-visible DOAS (3), fluorescence (4), chemiluminescence (7), solid-state sensors (1)
	NO_2	IR absorption spectroscopy (2), UV-visible DOAS (3), laser-induced fluorescence (4), chemiluminescence (after conversion, 7), sensors (after conversion, 1)
	NO_3	UV-visible DOAS (3), matrix isolation ESR (1), cavity ring-down spectroscopy (3), laser-induced fluorescence (4)
	N_2O_5	Cavity ring-down spectroscopy (3) or LIF after thermolysis to NO_3 and NO_2 (4)
	HONO	UV-visible DOAS (3), fluorescence (after conversion, 7)
	HNO_3	IR absorption spectroscopy (2), fluorescence (after conversion, 4), chemical ionisation mass spectrometry (5)
	Sum NO_y	Fluorescence (after conversion, 4), chemiluminescence (after conversion, 7)
	HO_2NO_2	Fluorescence (after conversion, 4), chemical ionisation mass spectrometry (after conversion, 5)
	Alkyl nitrates	Fluorescence (after thermolysis and conversion, 4), Chemical ionisation mass spectrometry (5), chromatography (8)
	PAN	Chemical ionisation mass spectrometry (5), gas chromatography with electron-capture detection (8)
	Other PANs	Chromatography (8)
	N_2O	IR absorption spectroscopy (2), gas chromatography (8)
	NH_3	IR absorption spectroscopy (2), UV-visible DOAS (3)
Halogenated compounds	HCl, HBr, HF	IR absorption spectroscopy (2)
	IO, I_2, OIO	UV-visible DOAS (3)
	BrO	UV-visible DOAS (3), fluorescence (after conversion, 4)
	OBrO	UV-visible DOAS (3)
	ClO	UV-visible DOAS (3), far-IR absorption spectroscopy (1), fluorescence (after conversion, 4)