Observations of trace gases in the earth's lower atmosphere: instrumentation and platform

L. K. Sahu[1,*], Nidhi Tripathi[1,2] and Ravi Yadav[3]

[1]Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India
[2]Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar 382 355, India
[3]Indian Institute of Tropical Meteorology, Pune 411 008, India

The earth's atmosphere is a complex mixture of many gases and their observations are incorporated in chemistry-climate models. Atmospheric observations have been the backbone of recent progress in atmospheric science, particularly about our understanding of the sun–atmosphere interaction causing chemical and radiative forcing linked to the environment and climate change. In terms of technology, there has been significant progress in both *in situ* and remote sensing measurements of several variables in the lower atmosphere. Among them, trace gases play an important role in climate change and several environmental problems. The recent progress in both *in situ* and remote sensing-based instrumentation has enabled researchers to study various atmospheric processes in great detail. For example, gas chromatography-based instrumentation provides detection from simple to complex species present in the atmosphere at very low concentrations. The laser-based spectroscopic instruments are emerging tools for fast response measurements of trace gases, which are important to understand rather short-term processes. The proton transfer reaction-mass spectrometry is regarded as one of the best technologies for the detection of numerous but specific types of trace gases, namely volatile organic compounds. However, there are advantages and disadvantages of any instrument in terms of quality of data, comprehensiveness and cost. In this article, we discuss the recent progress in instrumentation used for the measurement of trace gases in the lower atmosphere utilizing space, aircraft and satellite-based platforms as well as some laboratory techniques. We also briefly highlight the progress made during the past couple of decades, present status and future scenarios of trace gas measurements in the South Asia region.

Keywords: Climate change, lower atmosphere, remote sensing, trace gases.

We start with a fundamental question: what can we measure or observe in the atmosphere? Nitrogen (N_2) and oxygen (O_2) account for about 99% of atmospheric composition and other gases like argon (Ar), carbon dioxide (CO_2) and numerous trace gases contribute to just 1%.

Ironically, a majority of researchers are trying to understand the role of constituents which are less than 1% in the atmosphere. The concentration or mixing ratio of trace gases varies from parts per trillion (ppt) to parts per million (ppm) in the atmosphere. So what role do they play in the atmosphere despite their very low abundances? There are many important processes in the atmosphere where the role of trace gases can be highlighted. Nevertheless, one of the best known is the greenhouse effect in which some trace gases play a significant role in the warming of the atmosphere. The most abundant greenhouse gases (GHGs) in the atmosphere are water vapour (H_2O), CO_2, methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and chlorofluorocarbons (CFCs). The temperature of the earth's surface would be about $-18°C$ without the presence of GHGs in the atmosphere. However, the earth's actual average temperature is $+14°C$; therefore, warming by about $32°C$ is mainly due to the presence of GHGs in the atmosphere[1]. There are many other phenomena, such as the ozone hole in which the role of trace gases can be highlighted convincingly. Similarly, volatile organic compounds (VOCs), carbon monoxide (CO), and oxides of nitrogen ($NO_x = NO + NO_2$) are important trace gases which determine the local air quality and also play an important role in the global atmospheric chemistry[2]. VOCs have a high vapour pressure (>0.01 kPa at 20°C) and can easily enter into the atmosphere[3]. In the lower atmosphere, VOCs are known as precursors of O_3 and secondary organic aerosols (SOAs). Ozone and SOAs are produced from the oxidation of VOCs by hydroxyl (OH) radicals and follow-up reactions. Some VOCs such as benzene, toluene, ethylbenzene and xylene (BTEX) have a considerable adverse impact on human health and the environment, particularly in urban and industrial regions. Although some long-lived halogenated trace gases such as CFCs are present at low concentrations, they are known to have caused the global depletion of stratospheric ozone and the ozone hole over Antarctica. Similarly, there are many other trace gases which play an important role in the earth's atmosphere, and further discussion is beyond the scope of this article. Here we provide a brief overview of the recent progress in instrumentation used for the measurement of trace gases in the lower atmosphere using different observational platforms.

Objectives of atmospheric measurements

In general, the objectives of atmospheric measurements are not just to understand a few important effects or processes. The overall objectives will be better answered when we consider the following questions and their answers.

Q1. What is the use of atmospheric observations?
Ans. To understand the atmosphere and the processes broadly related to atmospheric chemistry and atmospheric dynamics.

Q2. Why is it important to understand these processes?
Ans. Because these processes in the atmosphere control our environment and play a role in climate change.

Q3. Why is continuous observation required?
Ans. Atmospheric processes are always changing, and to understand the cause of change and also to predict the changes, we need long-term and globally representative comprehensive observations. Here, we briefly discuss how different atmospheric processes work and control the distributions of trace gases in the lower atmosphere.

(a) Advection: This refers to horizontal motion in the lower atmosphere, which can transport pollutants from emission sources to great distances due to global wind circulations[4]. Intercontinental long-range transport of air masses takes a few days to a week of timescale. We use satellite and *in situ* observations to understand factors controlling the long-range transport of trace gases and the resulting impacts on regional climate and air quality.

(b) Convection: Convective transport can vertically redistribute the troposphere in less than 1 h (ref. 5). Atmospheric convection is an important phenomenon which particularly drives the weather and climate in the tropics and becomes a part of the global circulations.

(c) Photochemistry: This process refers to chemical reactions between different trace species in the presence of sunlight[6]. For example, the production of ozone in the troposphere is due to a set of reactions between precursor gases such as CO, oxides of nitrogen, VOCs, etc. The photochemical reactions are fast and transformations can take place in timescales of minutes to an hour. In any case, the combined effect of these three processes can be addressed using atmospheric models.

In the case of atmospheric measurements, we first need to know which trace gases are to be measured and why. Ideally, it depends on the objectives and priority; the World Meteorological Organization (WMO) has provided a comprehensive list of atmospheric composition, including trace gases to study the global climate change. The next question is regarding how these trace gases should be measured. For example, the radiosonde-based measurements provide high-resolution vertical profiles of many trace gases in the troposphere and stratosphere.

Satellite is another important platform which is unique for the global measurements of many trace gases. The ground-based measurements are used extensively for regional and long-term evaluation. However, we have listed three main challenges related to the measurements of trace gases.

(1) Levels of atmospheric trace gases can be very low: parts per trillion–parts per billion–parts per million. Therefore, developing sensitive instruments for the simultaneous detection of many trace gases is still a big challenge.

(2) Many important trace gases like O_3 and VOCs are very reactive and pose difficulties in storing and sampling for offline analysis. So we have to rely on on-line instruments which usually involve huge set-ups and are logistically difficult to carry around and operate in remote places. Nonetheless, atmospheric measurement programmes need to consider the fact that the atmospheric lifetimes of different trace gases vary in orders of magnitude, and hence govern the temporal and spatial distributions.

(3) Monitoring and observation networks at the ground level with stations have achieved good progress in some parts of the world, but are still insufficient to represent at global scales (not just integrated column, but vertically resolved measurements).

Measurements of trace gases have played an important role in the development of advanced instrumental techniques and platforms which provide key information about their levels and variability in the atmosphere. The three main challenges in the advanced measurement techniques are very low concentrations, high reactivity and aimed accuracy of about 10% or better.

In situ measurements

It is always important to review the advantages and disadvantages of existing atmospheric measurement systems before addressing future challenges. Several instruments have been developed and used to measure trace gas composition of the earth's atmosphere. Table 1 presents the operating method of instruments which are used for the measurements of trace gases and seasonal/annual mean of trace gases over the South Asia region[7–25]. Detailed studies of trace gases in India are reported in the literature[26–28]. An *in situ* measurement refers to the direct measurement using an instrument located within the atmosphere. The gas chromatography (GC) technique is regarded as one of the traditional methods used extensively for the measurement of many trace gases present at as low as a few parts per trillion in the atmosphere. GC is an analytical technique mainly used to separate the relatively unreactive trace gases. The GC-based separation methods exploit the distribution of the molecules between the mobile and stationary phases in the column. The mobile phase is a flow of chemically inert gases (e.g. He, Ar, N_2, etc.)

Table 1. List of trace gases and their measurement methods (*in situ*), and seasonal/annual mean mixing ratios reported at some urban/semi-urban/remote locations of India

Location	Gaseous species	Instrumentation techniques	Seasonal/annual mixing ratios (ppbv)	Reference
Ahmedabad (urban)	NMHCs, VOCs, OVOCs, CH_4, CO and O_3	PTR-TOF-MS, GC-FID, TD-GC-FID, spectroscopic instruments	O_3: 26.2 CO: 385 CH_4: 1.88 ppmv C_2H_4: 2.94 Winter OVOCs: 4.99–17.85	7–11
Udaipur (semi- urban)	O_3, CO, NO_x and NMVOCs	Spectroscopic instruments, TD-GC-FID	O_3: 22.4 CO: 343 NO_x: 11.5 C_2H_6: 4.38 C_5H_8: 1.12	12, 13
Delhi (urban)	NMHCs	GC-MS	Benzene: 12–55 $\mu g/m^3$ Toluene: 10–80 $\mu g/m^3$	14
Nainital (high-altitude)	O_3, CO and NO_y	Spectroscopic instruments/ analysers	O_3: 42 CO: 174 NO_y: 1455	15
Delhi (urban)	O_3, CO and NO_x during the commonwealth Games – 2010	Spectroscopic instruments/ analysers	Daytime O_3: 46.9 NO_x: 11.3	16
Chandigarh (urban)	NO_x, SO_2, O_3 and CO aromatic compounds during biomass burning event	Spectroscopic instruments/ analysers, automated on-line GC analyser	O_3: 22.5 CO: 1.5 ppmv NO_x: 12 SO_2: 7.5	17
Pantnagar (semi-urban)	O_3, CO and CH_4	Spectroscopic instruments/ analysers	O_3: 25 CO: 348 CH_4: 1.91 ppmv	18
Agra (urban)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 10–75 NO_x: 15–40	19
Kanpur (urban)	O_3, CO, NO_x and SO_2	Spectroscopic instruments/ analysers	O_3: 27.9 CO:721 CH_4: 5.7 SO_2: 3.0	20
Kannur (coastal)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 18.4 NO_x: 2.5	21
Gadanki (rural)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 9–37 NO_x: 0.5–2	22
Aizwal (semi-urban)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 18.2 NO_x: 9.1	23
Dibrugarh (semi-urban)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 16.25 NO_x: 15.2	24
Anantapur (semi-urban)	O_3 and NO_x	Spectroscopic instruments/ analysers	O_3: 40.7 NO_x: 5.1	25

which carry the analytes through the heated column. The analyte compounds, depending on the molecular structure or boiling point, are adsorbed differently in the stationary phase. Therefore, each compound elutes at a different time known as the retention time. Accuracy of GC-based analysis depends primarily on the efficiency of the column and the response of the detectors. The most common detectors are the flame ionization detector (FID), electron capture detector (ECD), thermal conductivity detector (TCD), flame photometric detector (FPD), nitrogen–phosphorous detector (NPD) and mass spectrometer (MS)[29]. Several types of detectors can be coupled with GC depending on the characteristics of the analytes of interest. In FID, the signal is generated from the ions produced from the combustion of trace compounds in a H_2-flame. In ECD, the electrons emitted by the radioactive foil (usually ^{63}Ni) ionize the analyte molecules. This detector is used widely for the detection of electron-absorbing
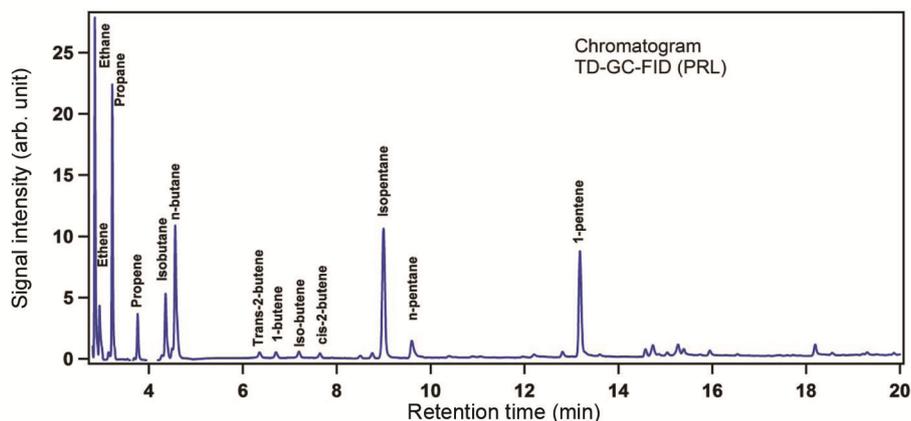
Figure 1. A typical chromatogram showing peaks of different non-methane hydrocarbons obtained from the analysis of ambient air using thermal desorption-gas chromatography flame ionization (TD-GC-FID) instrument at PRL, Ahmedabad, India.

components (high electronegativity) such as halogenated compounds. Depending on the molecule, an ECD can be 10–1000 times more sensitive than a FID. While in MS, the signal is generated from the electron impact ionization method or other ionization schemes (e.g. chemical ionization mass spectrometry (CIMS). This is an excellent and widely used instrument to study atmospheric composition as GC is capable of measuring numerous trace gases. There are certain disadvantages of GC-based instruments and one of them is the poor time resolution. For example, analysis of C_2–C_6 non-methane hydrocarbons (NMHCs) may take around 1 h, which includes pre-concentration of air samples. The pre-concentration technique allows the use of less-sensitive analytical methods for the measurement of trace gases that are present in the atmosphere at very low concentrations (pptv/ppbv). In the pre-concentration process, the analyte is adsorbed onto a sorbent and then released at high-enough concentrations into a smaller volume. The technique is mainly used in the GC-based method, making it applicable for the analysis of samples with very low concentration of trace gases. This order of analytical time resolution is not sufficient to study the short-timescale chemical and dynamic processes in the atmosphere. In other words, GC-based analysis does not provide truly continuous measurements and this is a key disadvantage. On the other hand, due to its high sensitivity and repeatability, the GC-based analysis is one of the best options for the long-term measurements of some trace gases like CH_4 and NMHCs. The GC-based systems have been used for semi-online monitoring and offline analysis of trace gases. Figure 1 shows a typical chromatogram obtained from ambient air analysis of NMHCs using thermal desorption (TD) coupled with the GC–FID system[7]. Advanced GC × GC methods can provide measurements of a vast number of species. At the same time, the requirements such as liquid nitrogen, ozone removal, adsorptive sampling, thermal desorption systems and the lack of skilled human resources limit the widespread use of such approaches in underdeveloped and developing countries.

Mass spectrometry is regarded as one of the most versatile analytical methods capable of identifying and detecting many different types of species in a single run. The GC coupled with MS (GC-MS) system has been extensively used for high-sensitivity measurements for many types of trace gases such as halocarbons, hydrocarbons and carbonyls compounds present in the atmosphere[30–33]. The mixing ratios of CFCs and HCFCs have been measured mainly using GC-ECD and also using GC-MS. Table 2 lists the important trace gases and their measurements, precision accuracy and limit of detection (LOD) using the GC-based method[34,35].

PTR-MS is a recent fast-response, but specific analytical technique used for measurements of a variety of VOCs present in the atmosphere. VOCs are important precursors of ozone and SOA production in the troposphere. In PTR-MS, the gas-phase hydronium (H_3O^+) ions are used as a reagent and VOCs are ionized by the transfer of proton (H^+). High mass- and time-resolution detection is one of the salient features of this technique. The PTR-MS with switchable reagent ions (e.g. H_3O^+, NO^+, O_2^+, etc.) is particularly useful for comprehensive measurements. Figure 2 shows a typical mass spectrum obtained from ambient measurements of VOCs at Ahmedabad city, Gujarat, India, using a high time- and mass-resolution proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS)[36]. PTR-MS can detect a large variety of VOCs, including oxygenated VOCs (OVOCs), while GC-based methods are mainly used for the measurement of CH_4 and NMHCs. GC-MS is a well-established method with a typical analytical time of ~1 h for the measurement of a comprehensive suite of species. Unlike the GC-MS, PTR-MS provides very high time-resolution (<1 s) for real-time measurements. The disadvantage of PTR-MS is that it cannot be used for the measurement of NMHCs (except a few compounds). In

Table 2. List of trace gases and their measurement precision accuracy and limit of detection (LOD) using the GC-based method

Compounds	Instrument	LOD (pptv)	Precision (%)	Accuracy (%)	Reference
C_2–C_5	GC-FID	3–5	1,3-Propylene: 30	1,5-Propylene: 20	
C_6–C_8	GC-FID	3	3	5	
α-Pinene	GC-FID	3	3	5	
β-Pinene	GC-FID	3	3	5	
Methyl bromide	GC-ECD	0.5	5	10	34, 35
Methyl iodide	GC-ECD	0.005	5	20	
Methyl chloride	GC-ECD	50	5	10	
Dichloromethane	GC-ECD	1	5	10	
Carbonyl sulphide	GC-ECD	10	2	10	
Dimethyl sulphide	GC-ECD	1	10	20	
Carbonyl sulphide OCS	GC-MSD	1	10	20	
Suite of VOCs	PTR-TOF-MS	1–20	2	15	36
	PTR-MS	0.2–1	5	15	
	GC-MS	0.2–20	5	15	
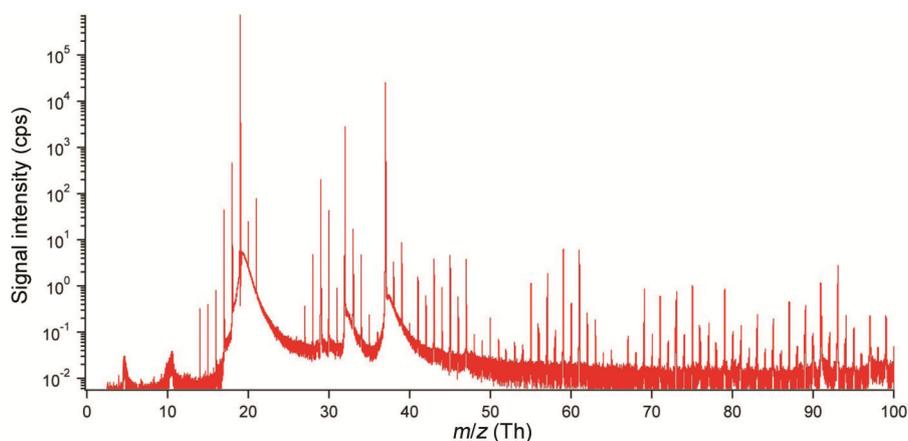
Figure 2. A typical mass spectrum obtained from ambient air measurements of volatile organic compounds using PTR-TOF-MS with hydronium ion (H_3O^+) as a reagent in Ahmedabad, during the winter season of 2014. The baseline underneath the peaks represents the background ions and electronic noise in the PTR-TOF-MS spectra. The bumps in the baseline signal are due to major primary ions (H_3O^+, H_2O–H_3O^+) and impurities (e.g. O_2^+, NO^+, NH_4^+). Before integrating the signals of different masses, baseline correction is performed by finding the signals at the middle points of two adjacent masses and interpolating using polynomial fits over the measured range.

addition to higher costs, PTR-MS is a bulky instrument with complex configurations and requires skilled operators to process the data. Nevertheless, both methods supplement each other and are being widely used for the measurement of trace gases in ambient air[37]. The PTR-MS system has also been used for flux measurements of VOCs using the eddy covariance method due to its excellent time response. In addition to relatively high costs, the operation and maintenance of mass spectrometers need trained human resources, and therefore, many laboratories cannot afford such instruments.

The spectroscopic analyser is another category of instrumentation used for the online *in situ* measurement of trace gases. In a spectroscopic analyser, the concentration of trace gases is determined based on the Beer–Lambert absorption law by relating the spectral absorbance of trace gases to their concentrations. The measurement of ground-level concentration of important trace gases

such as O_3, CO, NO, NO_2, SO_2, etc. is performed using on-line spectroscopic analysers with photometers as a detector. The spectroscopic analysers for online *in situ* measurement of trace gases mostly use the infrared (IR) or ultraviolet (UV) absorption photometry. For example, the detection of CO and O_3 is based on the absorption/attenuation of wavelengths of 4.7 and 254 nm respectively. The three main elements of online analysers are the light source (lamp), absorption cell and detector (mostly a photodiode). A good time-resolution and straightforward operation are the main advantages of online analysers. However, such analysers require a relatively large volume of air samples with high concentration. Therefore, detection at very low concentrations (pptv levels) may not be so accurate due to higher LOD. Measurements of many trace gases, particularly VOCs, using spectroscopic analysers are not being reported due to their weaker spectral features.

The recent detection technologies, mostly based on laser spectroscopy, are particularly used for the measurement of reactive and short-lived gases and radicals in the atmosphere. For example, hydroxyl radical (OH) cleanses the atmosphere of harmful trace gases. In the past, direct measurements of OH were challenging, mainly due to a short atmospheric lifetime of ~1 s. Three techniques, namely CIMS, laser-induced fluorescence (LIF), and differential optical absorption spectroscopy (DOAS) have been used for the measurement of several atmospheric radicals[38,39]. This is a unique technique, but disadvantages include high cost and complex configuration for the operation during field campaigns at remote locations. Other techniques used for the fast-response *in situ* measurements of trace gases include the tunable diode laser spectroscopy (TDLS)[40], photoacoustic spectroscopy (PAS)[41], and cavity ring-down spectroscopy (CRDS)[42], etc. The measurement principle using CRDS is based on the reduction in time constant as the rate of decrease of signal intensity is related to the number density of absorbing trace species. In TDLS, the concentration of target gases (e.g. NH_3, CH_4, CO_2, H_2O, HCl, etc.) is measured by absorption of radiation in the near-IR band generated by a laser diode. Absorption of IR light with trace gases in the cavity/measurement cell leads to the attenuation of intensity on the detector depending on the concentration. In the PAS system, gas molecules are excited from the ground to higher states by IR light. Subsequently, the non-radiative decay of excited molecules generates heat variation leading to a change in pressure depending on the concentration of target molecules. The PAS system has been used to measure stack gases and air pollutants emitted from the vehicular exhaust. However, the effective and widespread uses of advanced techniques such as PTR-MS, LIF, CRDS, etc. are constrained by associated higher costs and lack of trained human resources.

Remote sensing observations

So far, we have discussed the *in situ* measurements which are used for extensive local and regional climate change studies. But the ultimate goal is to study the global climate change for which the measurements should represent both vertical and horizontal distributions. Therefore, researchers not only rely on different types of instruments but also use different platforms for the operation. Remote sensing is the only technique which allows broad spatial coverage and frequent measurements[43]. In principle, the remote sensing methods provide the near-global coverage of various trace gases in the earth's atmosphere, but have limitations in vertical and temporal resolution[44]. The importance of space-based observations of tropospheric trace gases has been reported earlier[45]. There are two types of remote sensing: first is active in

which radiation is generated within the sensor, and the other is passive in which radiation comes from external sources such as the sun. The essential elements of a remote sensing system include a platform to hold the instrument (satellite-, ground-, aircraft-based), a target or object (in this case, atmospheric composition), and an instrument or sensor (mostly a high-resolution spectroscopic detector). The aircraft-based measurements of trace gases during take-off and landing provide their vertical profiles in the troposphere. For example, the vertical profiles of O_3 and CO from the Measurement of OZone and water vapour by in-service AIrbus airCraft (MOZAIC) measurements over Delhi, Chennai and Hyderabad airports were examined to understand seasonal and year-to-year variations[46–49]. For the global or large spatial scale, the remote sensing detection is performed from orbital platforms using instruments that detect electromagnetic radiation reflected or emitted from the atmosphere. Although most remote instruments use the same basic principle, the quality of the data depends upon the radiometric, spatial, spectral and temporal resolutions. Remote sensing of trace gases exploits their spectral features mostly in the IR, visible (VIS) and UV bands. Some recent satellite-based sensors to measure the abundances of trace gases in the lower troposphere include the Global Ozone Monitoring Experiment (GOME-2) for O_3, HCHO, NO_2, BrO, SO_2; SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) for O_3, HCHO, NO_2, SO_2, CO, CO_2, CH_4; Atmospheric Infrared Sounder (AIRS) for CO, CO_2, O_3, CH_4; Technology Experiment Satellite (TES) for O_3, CH_4, CO; Measurements of Pollution in The Troposphere (MOPITT) for CO, and Greenhouse Gases Observing Satellite (GOSAT) for CO_2, CH_4 respectively[50]. The horizontal resolution (repeat time) of AIRS, TES, SCIAMACHY, GOME-2, MOPITT and GOSAT was determined to be 13.5 km diameter (daily), 5×8 sq. km (6 days), 30×60 sq. km (6 days), 40×80 sq. km (6 days), 22×22 sq. km (3 days) and 10 km diameter (3 days) respectively. However, satellite-based measurements have specific advantages as they provide global observations. But the key disadvantages include the retrieval of integrated or column concentrations and not the well-resolved vertical concentration profiles[51]. The low-earth orbit (sun-synchronous and precessing), geostationary orbit (GEO), and Lagrange-1 (L1) orbit are recommended for future tropospheric trace gas measurements[52]. As mentioned earlier, the spectroscopic detections of many trace gases are not possible due to weak spectral features. Nevertheless, some VOCs such as formaldehyde (HCHO) are measured using satellite-based remote sensing. Another approach to measure tropospheric concentrations of some trace gases from ground-based UV/Vis remote sensing is Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS). This technique uses scattered sunlight as the light source to derive column

amounts of absorbing trace gases like nitrogen dioxide, glyoxal (CHOCHO), HCHO, H_2O, nitrous acid (HONO), etc. The spatial distribution of trace gases near the MAX-DOAS instrument can be derived by combining the measurements in different viewing angles. The ground-based MAX-DOAS is highly sensitive to trace gases in the boundary layer where concentrations are relatively high. The application of MAX-DOAS provides differential slant column densities by combining the observations with radiative transfer models[53]. Some trace gases like H_2O, CO_2, CH_4, O_3 and N_2O have strong spectral features in the near to mid-IR. The open-path laser sensing using light detection and ranging (LIDAR) system or the differential absorption LIDAR (DIAL) and Fourier transform infrared (FT-IR) spectroscopy is used to derive profiles of several important trace gases by measuring the slant column densities at various angles[54,55].

Landmark experiments

Concentration of CO_2 in the atmosphere has been found to increase continuously due to the ever-increasing use of fossil fuels for energy generation. The measurement of CO_2 at Mauna Loa, Hawaii, USA, constitutes the longest record of direct measurements of the gas in the atmosphere. The measurement of CO_2 at Mauna Loa was started by David Keeling of the Scripps Institution of Oceanography, USA, in March of 1958. Another landmark observation is the discovery of the ozone hole over Antarctica. In May 1985, Farman *et al*. from the British Antarctic Survey described their observations of large losses of ozone over Antarctica during October using the Dobson Ozone Spectrophotometer. The discovery of the ozone hole was possible only through the measurements. In the past 2–3 decades, many extensive experimental campaigns have been conducted to understand the regional chemistry and transport over different parts of the globe. But in the case of reactive trace gases like VOCs, measurements are being reported in the past 1–2 decades and for limited regions of North America and Europe. As shown in Figure 3, researchers have used various possible and innovative platforms for the measurement of trace gases which include balloon, satellite, international space station (ISS), aircraft, ground-remote, ground-*in situ*, ship-borne, unmanned aerial vehicle (UAV), etc. during most of such major campaigns. A discussion on the present and future requirements for the atmospheric observation system can be found in Laj *et al*.[56].

Current knowledge and challenging national and international issues

The physical and chemical properties of trace gases in the earth's atmosphere have been well established in terms of their impact on atmospheric chemistry and climate change. It is not just the average levels of various trace gases, but information on spatio-temporal variability is also critical to assess their roles in the atmosphere. The long-term continuous measurements of trace gases have been recommended by the Global Observing System (GOS) and the Global Atmosphere Watch (GAW) programmes of the WMO. For 5–6 decades, global researchers have been able to address both the issues of technological advancements and their operations to obtain quality measurements. However, global impact assessments in the chemistry-climate model require a realistic representation with details of the global spatio-temporal variations. The satellite-based measurements provide only broad features or an overview just for some limited number of species, but lack in providing accurate concentrations with details of local diurnal information. Nonetheless, researchers from across the world have been making a concentrated effort through various national and international programmes to achieve the goals of synergetic measurements of many trace gases. For example, the International Geosphere Biosphere Programme (IGBP) has been promoting global change studies since year 1987 (http://www.igbp.net/). The International Global Atmospheric Chemistry (IGAC), Integrated Land Ecosystem–Atmosphere Processes Study (iLEAPS), and Surface Ocean–Lower Atmosphere Study (SOLAS) are the major IGBP projects for the study of trace gases in the lower atmosphere. These projects formulate the guidelines and protocols for measurements of trace gases in the lower atmosphere at local, regional and global scales. One of the mandates of the WMO (a specialized agency of the United Nations) is to support and provide the guidelines for station-based long-term measurements of trace gases
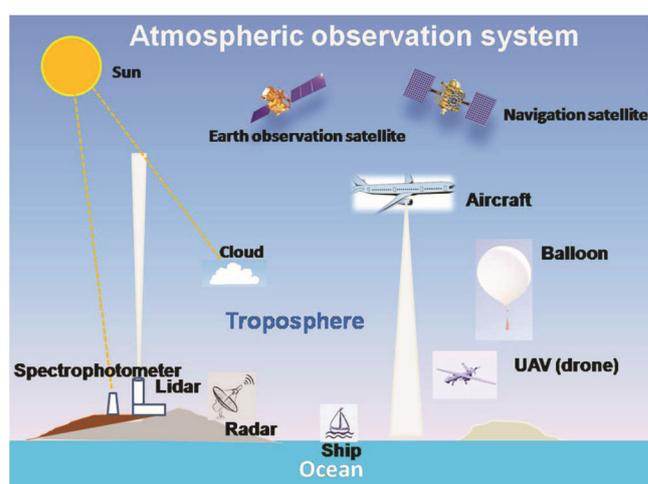

Figure 3. A pictorial representation of the atmospheric observation system consisting of a multitude of individual surface-, air-, and space-based instruments used for the *in situ* and remote sensing measurements of trace gases in the lower atmosphere. The integrated national and international strategies will be necessary to make comprehensive measurements of trace gases in the earth's lower atmosphere.

across the globe (https://public.wmo.int/en). The GAW programme was initiated in the 1960s to study the variability and trends in atmospheric composition and related physical parameters. The Global Climate Observing System (GCOS) and Global Observing System (GOS) coordinate and facilitate measurements of environmental observations, including trace gases. Different countries or unions have their dedicated agencies and programmes, such as the National Center for Atmospheric Research (NCAR), National Aeronautics and Space Administration (NASA) and National Oceanic, and Atmospheric Administration (NOAA) in the USA, and the Atmospheric Composition Change: a European NeTwork (ACCENT) of the European Union.

Despite significant advancements, there are regional gaps in terms of comprehensive measurements of trace gases. South Asia is geographically a vast region with different climatic conditions, where emissions of various gaseous species from both anthropogenic and natural sources make a significant contribution to the global budget. The climate of South Asia is tropical, where atmospheric fast chemical processes coupled with strong seasonal dynamics are complex and of great importance to global atmospheric chemistry. At a few stations in India, the monitoring initiatives date back to 1950s (refs 57, 58). In the past decades, most of the measurement programmes were initiated and sponsored by the Indian Space Research Organisation-Geosphere Biosphere Programme (ISRO-GBP). Although not exhaustive, measurements of trace gases (mainly O_3 and CO) conducted during the past several decades in India are reported in Lal[59]. Progress has also been reported in other countries like Pakistan, Nepal and Bangladesh of the South Asia region. In recent years, not only the ISRO-GBP but other agencies or ministries of India like the Council of Scientific and Industrial Research, Central Pollution Control Board, Ministry of Earth Sciences (MoES), Ministry of Environment and Forests, Department of Science and Technology, India Meteorological Department, etc. have been sponsoring and facilitating proposals related to trace gas studies in the country and the surrounding marine regions. Nonetheless, the observational networks established in the past two decades have yielded important information to the level, diurnal and seasonal variability of trace gases, but mostly of O_3 and CO. Satellite retrievals of a few trace gases have been utilized to fill the gaps for data-void regions. However, accurate measurements are inhibited mainly due to thick cloud coverage over South Asia.

In the South Asia region, the existing *in situ* measurement capacities of trace gases are mainly based on the infrastructure provided at the national level. Despite accelerated monitoring efforts, the networks are not dense enough to study spatial and temporal variations of trace gases in South Asia[60]. The long-term measurements of long-lived trace gases, mostly GHGs, have been reported

for different regions. Moreover, the measurement programmes of important reactive trace gases like VOCs and RHCs are preliminary and limited to a few stations[61,62]. Currently, the lack of adequate measurement technologies makes it difficult to pinpoint the influencing factors and the effects of climate change in a certain manner. There are several challenges to achieve the desired goals in terms of the measurement of trace gases over South Asia, but the two major challenges are related to the lack of infrastructure and expert researchers (both technical and scientific). In addition to capacity-building activities, the Government agencies and stakeholders must support the sustained and comprehensive measurement programmes of trace gases on a priority basis. The deployment of state-of-the-art instruments, without a team of experts, will make little contribution towards comprehensive measurement programmes. Therefore, there is a need to evolve collaborative programmes where high-quality *in situ* data from some available advanced instruments are to be supplemented or integrated with the data measured by a scattered group of researchers for wider and holistic representations. In terms of comprehensive measurements of trace gases involving only a few individuals or a small group of scientists are the limitations. On the other hand, the atmospheric measurement programmes offer excellent opportunities for efficient collaborations among different experts. The involvement of early-career scientists from developing countries like India in various national and international measurement programmes will add to the capacity building for conducting high-quality measurements of trace gases.

Summary

Measurements of trace gases are important to understand various processes in the atmosphere. The validation of regional and global models requires accurate measurements related to the variability of atmospheric trace gases. A wide range of equipment is being used by researchers for chemical speciation and high time-resolved detection of many different types of trace gases. At the same time, the measurement of atmospheric trace gas involves technological challenges, particularly for constituents at mixing ratios as low as a few ppt. However, it is desirable to achieve near-simultaneous measurements of many trace gases with high temporal, spatial and molecular resolution. In addition to a specific method, the integrated observations using satellites, ground-based measurements, ships, aircraft, balloons, etc. are important for comprehensive regional understanding. Although there exist long-term observations of some GHGs, there is a need to study the trends of reactive gases like VOCs in different regions of the world. Both *in situ* and ground-based remote sensing instruments have been useful for the long-term measurements. There is significant progress

in understanding the distribution of trace gases emitted from anthropogenic sources, but detection methods to quantify the biosphere–atmosphere exchange of trace gases need further improvements. The surface-level measurements have made progress, but vertical profile measurements of trace gases are limited to some specific regions of the world. The ground-based measurements will enable us to study both short- and long-term variability of trace gases and the role of the seasonality of emissions and photochemistry in the atmosphere. The airborne and ship-borne measurements provide spatial information of trace gases at the surface and different height layers respectively. The vertical measurements in the troposphere using airborne *in situ* and ground-based remote sensing systems are important to understand the impact of long-range and intercontinental transport. In the South Asia region, the measurement programmes of reactive trace gases are potentially crucial due to the lack of data. However, the uncertainty in future climate scenarios resulting from different models associated with trace gases is mainly due to improper constraining and parameterization. Therefore, the model approach to make predictions should rely on ground-truthed data. The regional trace gas data can be used to validate the chemistry and transport models. Measurements in the urban and polluted regions will provide necessary data to frame the policies controlling air quality and climate change on regional scales as several trace gases and their by-products are important criteria pollutants in different environments. In addition to addressing several key scientific issues, the final products should also contribute to policy-makers and the general public.

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