USING GROUND-BASED UV-VIS-IR SPECTROSCOPY TO PROBE ATMOSPHERIC COMPOSITION OVER CANADA

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Measurements are the life-blood of any attempt to understand atmospheric change. High-quality trace gas time series are essential for identifying and understanding the chemical and physical processes that underpin prediction through modelling. The importance of long-term data sets is increasingly recognized, most recently in the 2016 US National Academy of Sciences report on "The Future of Atmospheric Chemistry Research", which noted "*the central importance of long-term research sites for comprehensive atmospheric chemistry research*" [1]. This is particularly true in the Arctic, where the collection of such data can be challenging. For example, in 2015, a report by the Arctic Monitoring and Assessment Programme stated that "*Long-term monitoring of atmospheric composition at existing stations needs to be continued and integrated into a Pan-Arctic observation network*" [2]. Ground-based spectrometers provide a powerful tool for acquiring such measurements.

Canada has a long history in atmospheric remote sounding, with internationally recognized expertise in ultraviolet (UV), visible, and infrared (IR) spectroscopy [3]. Ground-based measurements of NO_2 using a grating spectrometer date back to the work of Alan Brewer and his colleagues at the University of Toronto [4]. This work led to the development of the Brewer spectrophotometer at Environment Canada, which is now deployed at about 80 stations worldwide for accurate measurements of ozone and UV radiation. Over the past 15 years, several new UV-visible and Fourier transform infrared (FTIR) spectrometers have been deployed in Canada for studies related to ozone, air quality, and climate. This article describes measurements and some science results from the University of Toronto Atmospheric Observatory (TAO, 43.66°N, 79.40°W) located in downtown Toronto, and from the Polar Environment Atmospheric Research Laboratory (PEARL, 80.05°N, 86.42°W) located in the high Arctic at Eureka, Nunavut [5]. Two case studies, one of biomass burning and one of stratospheric ozone depletion, are also presented.

SUMMARY

This article describes the use of ground-based UV-visible and Fourier transform infrared spectroscopy to measure atmospheric composition, with a focus on urban and Arctic sites.

FTIR SPECTROSCOPY

Infrared spectroscopy provides a valuable technique for measuring the concentrations of atmospheric constituents, and has been used for this purpose, from the ground, balloons, and aircraft, since the 1960s. Fourier transform infrared spectrometers have several advantages, including high spectral resolution, wide spectral coverage, and excellent throughput, which enable many species to be measured simultaneously. FTIR spectrometers are used to retrieve vertical columns and some vertical profile information using solar infrared absorption spectroscopy at several dozen sites worldwide, under the auspices of the Network for the Detection of Atmospheric Composition Change (NDACC) [6] and the Total Carbon Column Observing Network (TCCON) [7].

In Canada, there are currently two stations having FTIR spectrometers affiliated with these networks (Toronto and Eureka), with seven more instruments in use or available for deployment; several of which were part of the Canadian FTIR Observing Network (CAFTON). At TAO, we have an ABB Bomem DA8 spectrometer, which has been operational since 2002 and has undergone certification to become an NDACC instrument [8]. At PEARL, we have a Bruker IFS 125HR that currently alternates between NDACC and TCCON operations [9]. It was installed in 2006, replacing Environment Canada's Bomem DA8, which began making spring and some fall measurements at Eureka in 1993 [10]. Figure 1 shows the PEARL FTIR system, including the spectrometer and solar tracker. For both instruments, the main component is a Michelson interferometer, which is optically coupled to a solar tracker and records infrared solar absorption spectra during clear-sky daylight hours, typically achieving 80-120 observation days per year. NDACC spectra are recorded in the mid-infrared (750-4400 cm^{-1}) at high resolution (0.004 cm^{-1}) using a KBr beamsplitter, InSb and HgCdTe detectors, and a set of narrow-band optical interference filters. TCCON

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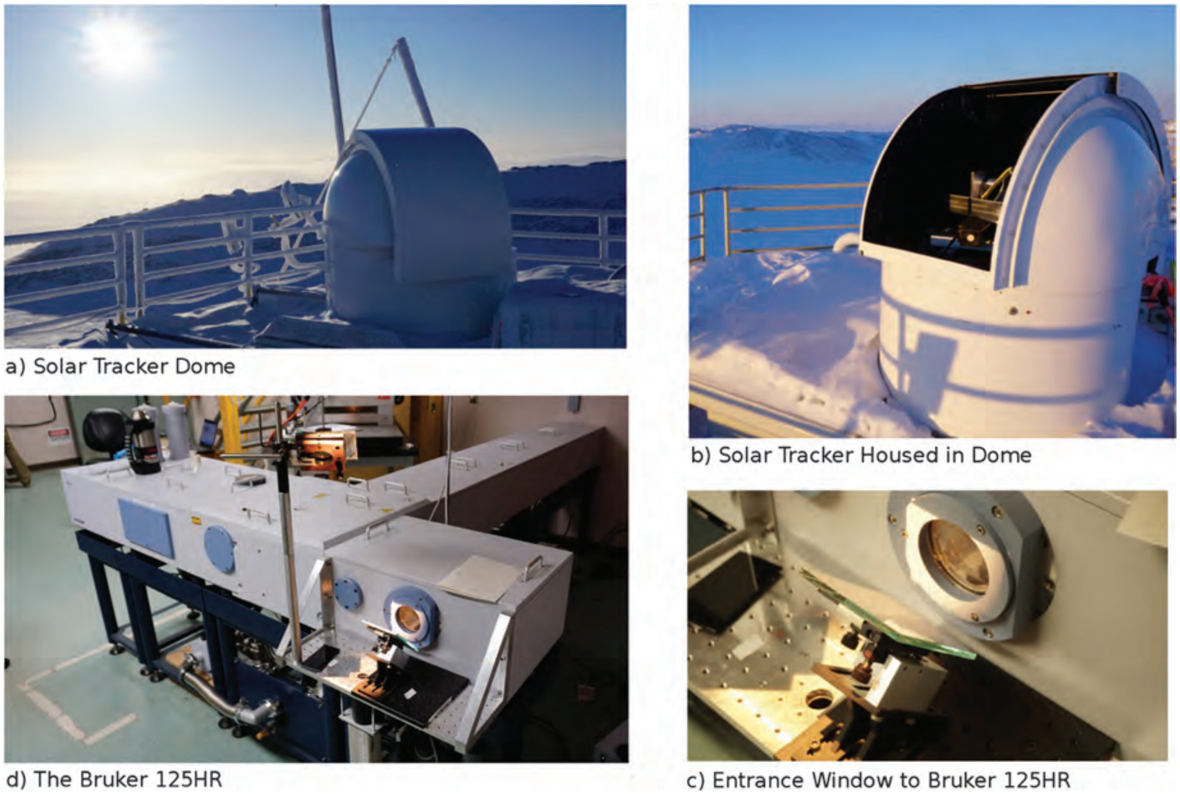
a) Solar Tracker Dome
b) Solar Tracker Housed in Dome
d) The Bruker 125HR
c) Entrance Window to Bruker 125HR

Fig. 1 The PEARL FTIR spectrometer and solar tracker system at Eureka.

spectra are recorded in the near-infrared (3800-11000 cm^{-1}) at 0.02 cm^{-1} resolution using a CaF_2 beamsplitter and InGaAs detector.

In addition to these two network-affiliated instruments, there are DA8 spectrometers installed at Environment and Climate Change Canada's (ECCC's) Centre for Atmospheric Research Experiments (CARE) at Egbert, Ontario, and at the Dalhousie Atmospheric Observatory in Halifax [11], an ABB Bomem Extended-range Atmospheric Emitted Radiance Interferometer (E-AERI) at PEARL [12,13], and the portable ABB Bomem Portable Atmospheric Research Interferometric Spectrometer for the Infrared (PARIS-IR) [14]. A new boreal TCCON site is also being established at East Trout Lake, Saskatchewan by Debra Wunch (University of Toronto), and horizontal long-path systems are being set up at Halifax [15] and Toronto for boundary layer measurements.

For both the PEARL and TAO NDACC measurements, spectra are processed using the SFIT4 retrieval algorithm (https://wiki.ucar.edu/display/sfit4/), widely used by the NDACC FTIR community. SFIT4 is based on the optimal estimation method [16], which combines a priori information with information contained in the spectral measurements. A line-by-line radiative transfer model is used as the forward model to calculate absorption spectra of the trace gas of interest given temperature, pressure, and a priori volume mixing ratio (VMR) profiles and spectroscopic line parameters. The a priori VMR profile is iteratively adjusted until convergence is reached and the difference between the measured and calculated spectra is minimized. The retrieved VMR profiles can be converted to density profiles using temperature and pressure profiles and integrated to yield total and partial column densities. Numerous trace gases have been retrieved from our FTIR spectra, including O_3, HF, HCl, HNO_3, NO, NO_2, and $ClONO_2$, for stratospheric studies, and N_2O, H_2O, HDO, CO, OCS, CH_4, C_2H_6, C_2H_2, HCN, HCHO, CH_3OH, and HCOOH for tropospheric science. For PEARL TCCON spectra, the GFIT nonlinear least-squares spectral fitting algorithm is used; the general approach is similar but the a priori profile is scaled to obtain a profile that is converted into a total column and then into a column-averaged dry-air mole fraction using the retrieved column of O_2 [7], with CO_2 and CH_4 being the two primary data products.

UV-VISIBLE SPECTROSCOPY

The measurement of atmospheric constituents using UV-visible differential optical absorption spectroscopy (DOAS) is a well-proven and widely used technique, also included in NDACC. Spectra are recorded over a wide spectral range, allowing simultaneous detection of several gases, while the DOAS approach of ratioing spectra to a reference spectrum eliminates solar lines, the instrument response function, and smoothly varying features such as Rayleigh and aerosol scattering, allowing the detection of very weak absorptions. Historically, ground-based UV-visible spectrometers made measurements of scattered sunlight using zenith-sky viewing geometry [17,18]. With this technique, sunlight traverses a long path through the stratosphere, but only a short path through the troposphere, enhancing the relative contribution of stratospheric absorption. In recent years, multi-axis DOAS (MAX-DOAS) has been successfully applied to retrieve trace gas concentrations in the troposphere from spectra of scattered sunlight measured over a range of elevation angles above the horizon [19].

We have two UV-visible instruments, the University of Toronto Ground-Based Spectrometer (UT-GBS) and the PEARL-GBS. These both include a Horiba/Jobin-Yvon Triax-180, which is a crossed Czerny-Turner triple-grating imaging spectrometer, coupled to a thermoelectrically cooled charge-coupled device detector. Depending on the choice of grating, spectra can be recorded over different spectral ranges at varying spectral resolution. As NDACC instruments, the GBSs use the zenith-sky DOAS technique. The UT-GBS was assembled in 1998 and deployed on the ground during the four Middle Atmosphere Nitrogen TRend Assessment (MANTRA) balloon campaigns [20-22]. It has also taken measurements at Eureka during polar sunrise from 1999-2001 and 2003-2016 (as part of the Canadian Arctic ACE/OSIRIS Validation Campaigns since 2004 [23]) and was permanently installed at PEARL in 2008, primarily operating in the visible for measurements of ozone and NO_2. The PEARL-GBS is a newer instrument that was installed inside at PEARL in August 2006 [24] and primarily works in the UV for measurements of BrO and OClO. With the later installation of solar trackers, the instruments were upgraded in 2011 (PEARL-GBS) and 2015 (UT-GBS) to enable MAX-DOAS measurements.

The relative portability of UV-visible spectrometers makes it possible to conduct intercomparison campaigns to assess their performance and improve measurement strategies. In 2009, the UT-GBS participated in the Cabauw Intercomparison of Nitrogen Dioxide Measuring Instruments (CINDI), an NDACC campaign held in the Netherlands [25]. This was followed by the CINDI-2 campaign in September 2016, also held at Cabauw (http://www.tropomi.eu/science/cindi-2). The goal of this campaign was to characterize differences between the measurement approaches and systems used within the international DOAS community, and to work towards harmonisation of MAX-DOAS settings and retrievals in preparation for global validation of satellite missions focusing on air quality, such as the European Space Agency's upcoming Sentinel 5 Precursor. The PEARL-GBS was one of about 30 instruments participating in this initiative (see Fig. 2) and detailed comparisons are now underway.

COMPOSITION MEASUREMENTS

The troposphere is a chemically complex region of the atmosphere, where gases from natural and anthropogenic sources undergo transport and chemical processing on similar time scales. Measurements of atmospheric composition in the troposphere provide insight into issues related to air quality and climate change. Air quality is generally monitored by measurements of "criteria air contaminants" that are correlated with adverse health consequences. The chemical and dynamical relationships between these species and their precursors are complex and non-linear. Changes in anthropogenic emissions and climate will alter these relationships and the oxidizing capacity of the troposphere. While an urban location like Toronto is clearly subject to pollution events, the Arctic also experiences poor air quality due to transport from mid-latitudes.

Current research questions include the links between regional air quality and global atmospheric chemistry, the impact of climate change on air quality, production of ozone from tropical and mid-latitude emissions of precursors such as methane, transport pathways of pollutants into the Arctic, new sources of local pollution from shipping and oil/gas extraction, and deposition of harmful contaminants in snow. Arctic tropospheric ozone is greatly affected by severe surface ozone depletion events, first observed at Alert and since linked to extremely high concentrations of BrO in bromine explosion events. These are still not fully understood, but are important because they increase the deposition of mercury to snow, causing harmful effects on ecosystems and humans. Tropospheric ozone in the Arctic also acts a significant short-term climate forcer.

Meanwhile, increases in the concentrations of greenhouse gases are well documented, but "*Understanding the global carbon cycle, and predicting its evolution under future climate scenarios is one of the biggest challenges facing science today*" [26]. These challenges are due to lack of sufficient knowledge about carbon sources and sinks, feedbacks between climate change and carbon reservoirs, and anthropogenic emissions from fossil fuel burning and land use change. The issues are more acute at high latitudes where measurements are scarce and the magnitude and distribution of carbon sinks and sources are poorly known.

We are using trace gas measurements at Toronto and Eureka to address some of these scientific issues. The combined TAO/CARE FTIR dataset of HF, HCl, N_2O, and O_3 columns has been used to identify polar vortex intrusion events over Toronto, and establish a dynamical cause for some of the winter/spring variability of stratospheric trace gases observed at this mid-latitude site [27]. In another study, the GEOS-Chem 3-D chemical transport model was used to interpret the FTIR measurements of tropospheric O_3, CO, and C_2H_6, and to identify the sources of air pollution over Toronto [28]. Our FTIR data have been included in numerous multi-station studies; a few

Fig. 2 Remote sensing instruments performing measurements during the CINDI-2 campaign held at the Royal Netherlands Meteorological Institute's Cabauw site in September 2016. PEARL-GBS is inside the white box in the middle of the picture, with its tracking system mounted on top of the box.

examples include solar and lunar measurements of nitric acid compared with models [29], source attribution of Arctic pollution [30,31], CO_2 flux inversions [32], trends in HCl, $ClONO_2$, and HF [33], tropospheric water vapour isotopologues [34], global methane signals [35], sources and sinks of carbonyl sulfide [36], and detecting and attributing the recent rise in ethane and methane emissions to expansion of oil and natural gas extraction in North America [37]. Other studies have included the first detection of NO in the upper atmosphere by ground-based FTIR spectroscopy [38] and determination of the Arctic NOy budget [39]. The data have also been used to evaluate and improve atmospheric models [40,41], including ECCC's new Carbon Assimilation System [42]. DOAS measurements of BrO and ozone have been combined with satellite data to track a bromine explosion event transported from the Beaufort Sea to Eureka [43] and used to investigate the impact of the 2008 solar eclipse on ozone and NO_2 [44]. Measurements from both sites have also been used for validation of data products from

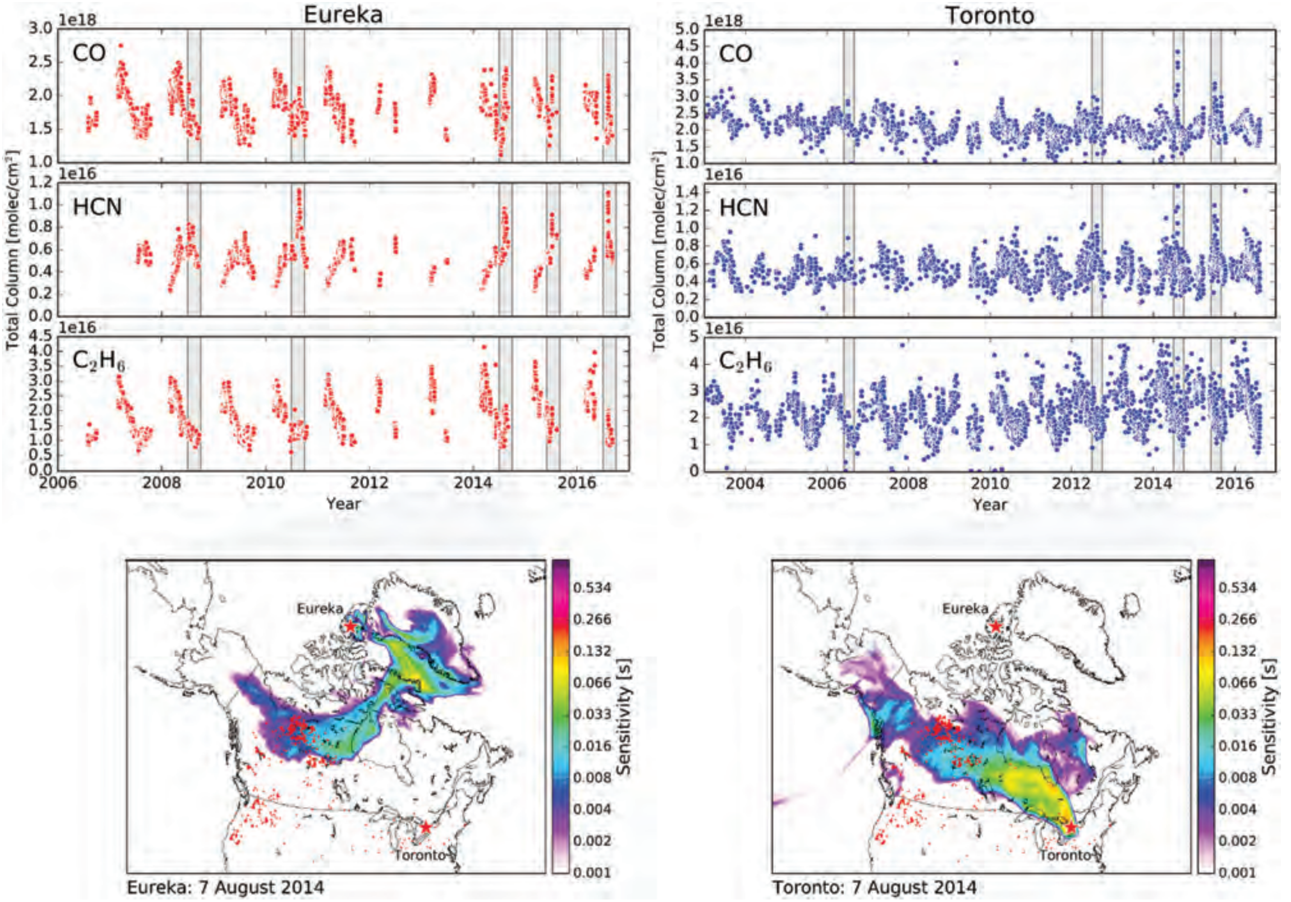

Fig. 3 Top panel: Time series of CO, HCN and C_2H_6 for Eureka (left, red) and Toronto (right, blue). Bottom panel: FLEXPART sensitivity of Eureka and Toronto measurements on August 7, 2014 to the Northwest Territories fires. The red points are the MODIS fire hot spots, indicating the location of wildfires.

Canadian (ACE-FTS and MAESTRO on SciSat, OSIRIS on Odin), American (OCO-2), European (SCIAMACHY on Envisat, IASI on MetOp), and Japanese (TANSO-FTS on GOSAT) satellite instruments.

DETECTION OF BIOMASS BURNING POLLUTION

One focus of attention over the last several years has been the detection of smoke plumes transported from forest fires and the derivation of emission factors. Biomass burning is a considerable source of trace gases and aerosols that can affect tropospheric chemistry and radiative balance. The Arctic is a major receptor to pollution from mid-latitude regions, including emissions from boreal fires. The influence of biomass burning is further complicated by the sensitivity of fire intensity and frequency to climate change and to land use practices. There have been some suggestions that wildfire activity in North America is increasing in response to climate change [45,46], but the interannual variability of biomass burning events and trends in emissions remain uncertain.

Trace gas measurements by FTIR instruments provide a means of detecting transport of biomass burning plumes into the Arctic where satellite and in-situ observations may be sparse. Emissions from boreal wildfires have been shown to contribute to the day-to-day variabilities of seven tropospheric species observed at Eureka [47]. In the time series presented in Fig. 3, the gray shaded regions highlight periods of fire-affected measurements for major biomass burning events. The species CO, HCN, and C_2H_6 are all emitted in large abundances from wildfires, and enhancements of their total columns were observed at Eureka in July-August 2008, 2010, and 2016 due to boreal fires in Russia. For Toronto, pollution from forest fires in Northern Ontario was detected in July 2006. Pollution was observed at both sites in July-August 2014 from wildfires in the Northwest Territories, and in June 2015 due to fires in Saskatchewan.

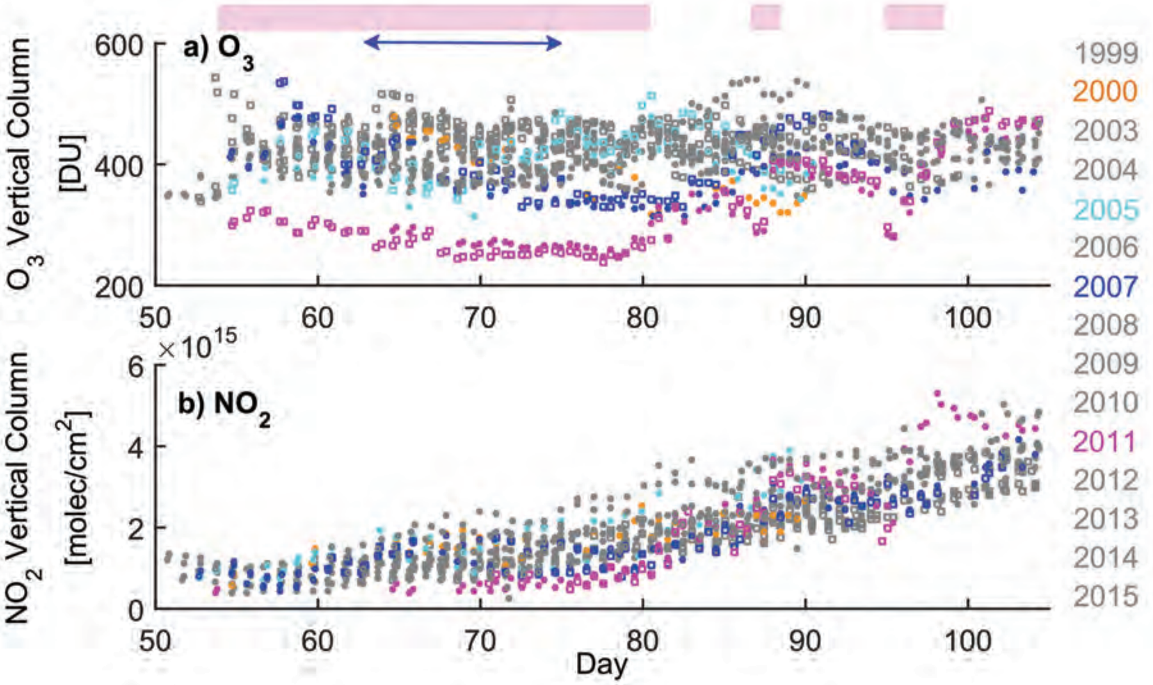

Fig. 4 Time series of zenith-sky DOAS measurements of ozone and NO_2 for 1999-2015 versus day of year. Year 2000 is shown in orange, 2005 in cyan, 2007 in blue, 2011 in magenta, and all other years are shown in grey. (a) Ozone total columns measured by the UT-GBS (closed circles) and SAOZ (open squares). The magenta bar at the top indicates periods when the polar vortex was above Eureka and the blue line indicates when temperatures were below the threshold for the formation of polar stratospheric clouds. (b) NO_2 partial columns (17 km to top of atmosphere) measured by UT-GBS (closed circles) and PEARL-GBS (open squares). SAOZ data courtesy of Florence Goutail and Andrea Pazmino, Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), France.

The long-range impact of wildfires is evident in the source attribution for each measurement site. An example is shown in Fig. 3 for the 2014 Northwest Territories fires. For each site, the Lagrangian particle dispersion model FLEXPART [48] is run backwards in time. A total of 60,000 air-tracer particles are released over a 6-hr period about the peak enhancement of CO at Eureka and Toronto. The model is then run backwards in time for 7 days. The residence time of the particles is proportional to the sensitivity of the measurement to various source regions. The fire locations are indicated by the Moderate Resolution Imaging Spectroradiometer (MODIS) fire hot-spots, plotted in red. For both sites, sensitivity of the measurements to the fires in the Northwest Territories is observed. Measurements of pollution are thus not only influenced by nearby sources, but also by long-range transport from distant sources; this is particularly important in the Arctic, a region isolated from local anthropogenic and biomass burning sources.

Using CO as a tracer of biomass burning emission, the measured ratio of the abundance of a trace gas species to the abundance of CO for fire-affected measurements is indicative of the emissions of the species at the fire source, which is dependent on the type of vegetation burned. This is referred to as the emission factor, which is the ratio of the abundance of a species emitted to the amount of dry matter burned. Precise emission factors are required for improved accuracy of atmospheric chemistry and climate models. FTIR measurements at Eureka and Toronto have been used to determine emission factors from boreal forests for HCN and C_2H_6 [49-51], as well as for other minor species including C_2H_2, HCOOH, CH_3OH and H_2CO [50], and NH_3 [51]. The latter are the first long-term measurements of ammonia in the High Arctic transported from wildfires.

ARCTIC STRATOSPHERIC OZONE DEPLETION

The PEARL Ridge Lab, which houses the FTIR and GBS instruments, was built by Environment Canada in 1992. It was originally named the Arctic Stratospheric Ozone Observatory, reflecting its scientific focus given the intense interest in polar stratospheric ozone after the discovery of the Antarctic ozone hole in 1985. Arctic ozone chemistry, in both the troposphere and the stratosphere, remains a subject of interest. While the Montreal Protocol and its amendments have reduced the production of ozone-depleting chlorofluorocarbons, their long lifetimes mean that stratospheric ozone depletion will continue for several decades. In the Arctic, there continues to be springtime ozone depletion, averaging 10-15% since 1980. At the same time, the impact of climate change on ozone is increasing, and there is considerable interest in the processes coupling stratospheric chemistry and climate, in the Arctic and globally. While increasing concentrations of CO_2 are cooling the stratosphere and thereby reducing global ozone loss rates, this cooling may generate more polar stratospheric clouds (PSCs) and enhance chemical ozone depletion in the Arctic. Springtime ozone depletion continues in this region, with significant interannual variability driven by atmospheric dynamics, transport, and temperature. Chemistry-climate models predict that springtime Arctic ozone will recover to 1980 values between 2025 and 2035, with the evolution of the ozone layer in the late 21st century strongly influenced by atmospheric abundances of CO_2, N_2O, and CH_4 [52].

In 2011, PEARL observations captured the largest stratospheric ozone depletion event ever seen in the Arctic. This occurred exactly over PEARL, with about 40% of the ozone column destroyed due to the stable vortex and very low stratospheric temperatures. Eureka is an ideal location for stratospheric measurements, as the winter polar vortex regularly passes overhead, allowing measurements to be made under both chemically perturbed and unperturbed conditions; the site of the Ridge Lab was chosen for this reason. Both the PEARL FTIR and the GBS instruments measured unprecedentedly low ozone columns in spring 2011, when the polar vortex was typically circular, cold and centered above the pole, with Eureka mostly inside the vortex from October 2010 until late March 2011. Complementary measurements of unusually low HCl, NO_2, $ClONO_2$, and HNO_3 total columns, enhanced OClO columns, and lidar observations of polar stratospheric clouds above Eureka all indicated chlorine activation on cold aerosol particles followed by chemical ozone destruction [53,54].

As seen in Fig. 4, ozone columns measured by the GBSs and a similar System d'Analyse par Observations Zenithales (SAOZ) UV-visible spectrometer [55] were lower than in any other year between 1999 and 2015. In 2000, 2005, and 2007, the polar vortex was also overhead and low ozone and NO_2 columns were also observed. However, 2011 is notably different, with a maximum percent ozone loss of 47% or 250 Dobson Unit (DU, $1\ \mathrm{DU} = 2.69 \times 10^{16}$ molec cm^{-2}) derived from UT-GBS data on 5 April 2011. These measurements agree with photochemical model runs, which indicate that prolonged denitrification by sedimentation of polar stratospheric clouds delayed chlorine deactivation, leading to the record ozone loss [56]. Unusual conditions were also observed in late spring 2011, when a frozen-in anticyclone in the middle stratosphere above Eureka resulted in anomalous chemistry, enhancing the NO_2 VMR in this region and causing unusually large ozone loss in April/May compared with previous years [57]. Over the next few decades, while stratospheric chlorine and bromine loading remains high, similar ozone depletion events are expected to occur when dynamic variability results in an isolated polar vortex with persistently cold stratosphere [52].

CONCLUSION

Measurements of chemical constituents are essential for understanding atmospheric composition and its spatial and temporal variability, as well as the underlying chemical processes and the role of dynamical transport. Ground-based UV-visible and Fourier transform infrared spectrometers are capable of measuring several dozen atmospheric species over many years, providing data sets that can be used to address a wide array of scientific questions related to ozone, air quality, and climate. Such measurements have been made in Toronto and Eureka for over a decade and have contributed to improving our knowledge of atmospheric composition over Canada.

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TAO and PEARL data mentioned in this paper can be found at ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/toronto, ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/eureka/, and ftp://tccon.ornl.gov/2014Public/eureka01/R0_archive/.

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