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LETTER

Atmospheric trace gas trends obtained from FTIR column measurements in Toronto, Canada from 2002-2019

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Abstract

Total columns of C2H2, C2H6, CH4, CH3OH, CO, H2CO, HCl, HCN, HCOOH, HF, HNO3, N2O, NH3 and O3 were retrieved from 2002-2019 using a Fourier transform infrared (FTIR) spectrometer at the University of Toronto Atmospheric Observatory (TAO). Trends and enhancement events were determined by fitting trended Fourier series, and bootstrapping was used to identify the statistical significance. Trends from 2002 to 2019 (%/year, with 2σ uncertainties) were found for C2H2 (−1.12 ± 0.30), C2H6 (−0.74 ± 0.73 from 2002–2008 and 1.19 ± 0.27 from 2009–2019), CH4 (0.26 ± 0.10 from 2002–2008 and 0.41 ± 0.03 from 2009–2019), CO (−0.90 ± 0.07), HCN (−0.51 ± 0.21), HCOOH (−2.15 ± 0.64), HF (0.59 ± 0.11), HNO3 (0.36 ± 0.13), N2O (0.28 ± 0.02), NH3 (3.56 ± 0.85), and O3 (0.28 ± 0.19 and −0.05 ± 0.07 for tropospheric and stratospheric columns, respectively). The GEOS-Chem chemical transport model showed that wetland emissions were the largest contributor to CH4 columns measured at TAO (average relative contribution of 31.7%), and that CH4 oxidation was a major source of CO (accounting for 30.9%).

1. Introduction

Fourier transform infrared (FTIR) spectroscopy is a powerful tool for determining the concentration profiles and total columns of atmospheric trace gases. The FTIR spectrometer situated at the University of Toronto Atmospheric Observatory (TAO) has been making regular measurements since 2002 as a station in the Network for Detection of Atmospheric Composition and Change (NDACC) (De Mazière et al. 2018). Its location, in downtown Toronto, is downwind of biomass burning events (Lutsch et al. 2016, Yamanouchi et al. 2020a), as well as plumes from the USA and other regions of Canada (Whaley et al. 2015).

The 18-year time series of measurements at TAO are valuable for assessing trends of trace gas species such as nitrous oxide (N2O), methane (CH4), and ethane (C2H6) (Franco et al. 2016a, Tzompa-Sosa et al. 2017, 2019). FTIR spectroscopy is particularly useful, as a large number of species can be measured simultaneously. CH4 and N2O are two of the most powerful greenhouse gases (GHGs) in the atmosphere, and accurate concentration estimates are needed to model their climate change effects (IPCC 2014, NAS 2016). N2O, which primarily comes from microbial activity, has been increasing steadily, at about 0.26%/year (IPCC 2007) (estimated using surface measurements). A study by Angelbratt et al. (2011a) using FTIRs in Europe gave similar trends in N2O columns, although the N2O trend over Toronto using an FTIR spectrometer has yet to be investigated. N2O is also an important stratospheric ozone (O3) depleting gas (Ravishankara et al. 2009), and a recent study suggests that agricultural emissions of N2O have led to an increase in emissions faster than previously estimated by IPCC (Thompson et al. 2019).

CH4 is one of the GHGs targeted by the Kyoto Protocol, and keeping track of CH4 trends is necessary for understanding climate change (IPCC 2014). CH4 concentrations are increasing and it was suggested by Franco et al. (2016a) that increasing oil and gas production in North America is the source of the recent upward trend; they estimated that CH4 from oil and gas production increased by 15 Tg/year over the period from 2008 to 2014. Similarly, Turner et al. (2016) estimated that overall North America CH4 emissions have risen by over 30% over the period from 2002 to 2014. However, Bruhwiler et al. (2017) have pointed out that such claims are not
consistent with observations, and uncertainties regarding CH₄ trends still remain. Because C₂H₆ is co-emitted with CH₄ during oil and gas production, examining both species provides a tool for investigating sources, and there is evidence that C₂H₆ columns are also increasing (Franco et al. 2016a, Helmig et al. 2016). C₂H₆ is one of the most abundant non-methane hydrocarbons (NMHCs) in the atmosphere, and is of interest due to its possible link to CH₄ emissions, and because it, along with CH₄ and other NMHCs, is an important precursor to aerosols and pollutants such as tropospheric O₃ (Jacob 1999, Fiore et al. 2008).

Tropospheric O₃ is a pollutant and it, along with other trace gases like carbon monoxide (CO), are important indicators of air quality (Jacob 1999). Ground-level O₃ is regularly monitored in Canada, along with fine particulate matter, NOₓ, and CO, as they are considered to pose serious health risks. In Ontario, overall air quality has been improving, and only O₃ continues to exceed health standards set forth at the provincial level (http://www.airqualityontario.com/press/publications.php). Other pollutants measured at TAO include ammonia (NH₃) and CO. NH₃, in particular, has been linked to particulate matter formation (e.g., Viatte et al. 2019), and recent findings (e.g., Warner et al. 2016, Yamanouchi et al. 2021) suggest its abundance is increasing.

CO enhancement events are observed in TAO data, as Toronto is downwind of biomass burning events (e.g., Lutsch et al. 2016). Recent studies using the GEOS-Chem chemical transport model (CTM) has attributed CO enhancement events over Toronto to forest fires (Lutsch et al. 2020, Yamanouchi et al. 2020a). GEOS-Chem (Bey et al. 2001) can be run in a "tagged" tracer mode to trace specific chemical species back to sources. However, these tagged runs have yet to be utilized to identify sources in the trend of CO seen in Toronto; this is one objective of the work presented here.

TAO measurements also include acetylene (C₂H₂), which is primarily emitted from biofuel and fossil fuel combustion as well as biomass burning (Duflot et al. 2015); methanol (CH₃OH), which is known to be a major source of CO and formaldehyde (H₂CO) (Jacob et al. 2005); as well as H₂CO itself, which is an important air pollutant (Luecken et al. 2018). Other gases retrieved at TAO include HCl, a stratospheric gas and the largest chlorine reservoir (Mahieu et al. 2014); HCN, a key tracer specie for identifying biomass burning enhancements (e.g., Viatte et al. 2013); HCOOH, a gas known for its potential for increasing rain acidity as well as being one of the most abundant volatile organic compounds (VOCs) in the atmosphere; HF, which is a reservoir for stratospheric halogens (Cheng 2018), and HNO₃, an acidic pollutant that is a reservoir of NO₃ (Hanke et al. 2003).

There is a growing need for long-term observations in order to monitor atmospheric composition and its response to environmental change. Here we present the time series of 14 trace gases (C₂H₂, C₃H₆, CH₄, CH₃OH, CO, H₂CO, HCl, HCN, HCOOH, HF, HNO₃, N₂O, NH₃ and O₃) measured at TAO from 2002 to 2019, investigate their trends, discuss the statistical significance of these trends, and for CO and CH₄, use the GEOS-Chem CTM to identify major sources over Toronto. This is the first presentation of long-term trend analyses of C₂H₂, HCN, HNO₃, and N₂O total columns, and stratospheric and tropospheric O₃ columns from an FTIR over Toronto.

The rest of this paper is organized as follows: section 2 describes the retrieval methodology, the model used for analyses, and the methods used to obtain trends, as well as their limitations. Section 3 presents the 18-year time series and trends in total columns retrieved from the TAO FTIR spectra, along with a discussion on source attribution using the GEOS-Chem tagged CO and CH₄ simulation runs. The main conclusions are presented in section 4.

2. Methods

2.1. Instrument

Total columns of the trace gases used in this study were retrieved from infrared solar absorption spectra measured with a ABB Bomem DA8 FTIR spectrometer situated in the University of Toronto Atmospheric Observatory in downtown Toronto, Ontario, Canada (43.66° N, 79.40° W), 174 masl, which has been operational since mid-2002. Datasets used in this study are contributed to NDACC (http://www.ndsc.ncep.noaa.gov/). The DA8 has a maximum resolution of 0.004 cm⁻¹, with a maximum optical path difference of 250 cm. For this study, the FTIR was equipped with a KBr beamsplitter and InSb and HgCdTe detectors for a total spectral range of 700 to 4300 cm⁻¹. The DA8 is coupled to a sun-tracker that actively tracks the Sun during the day. The tracker was manufactured by Aim Controls and is driven by two stepper motors on elevation and azimuth axes. The active tracking was provided by four photo-diodes from 2002-2014, and was updated to a camera and solar-fitting Community Solar Tracker in 2014 (Franklin 2015). Further details of the system can be found in Wiacek et al. (2007). It should be noted that due to the nature of solar-pointing FTIR measurements, the measurements are limited to sunny days, resulting in gaps in the time series; spectra are typically measured on 100-150 days per year. The TAO FTIR uses six filters standardized by the NDACC Infrared Working Group (IRWG), and measures spectra through each filter in sequence.
Table 1. Microwindows for the TAO FTIR retrievals, mean retrieval errors, and mean DOFS. Mean values are for the entire 2002-2019 time series. The errors were calculated during the retrieval using the SIFT4 retrieval algorithm (see section 2.2 for more details on the retrieval).

| Species     | Microwindows (cm⁻¹)                                                                 | Mean random error(%) | Mean systematic error (%) | Mean total error(%) | Mean DOFS |
|-------------|-------------------------------------------------------------------------------------|----------------------|---------------------------|---------------------|-----------|
| C₂H₄        | 3250.4–3250.8, 3268.25–3268.75, 3304.7–3305.4                                        | 25.1                 | 8.8                       | 26.9                | 1.5       |
| C₂H₆        | 2976.77–2976.95, 2983.2–2983.35, 2986.5–2986.95                                     | 2.1                  | 4.3                       | 4.9                 | 1.9       |
| CH₄         | 2613.7–2615.4, 2835.3–2835.8, 2921.0–2921.6                                        | 2.0                  | 3.9                       | 4.4                 | 2.1       |
| CH₃OH       | 992.0–998.7, 1029.0–1037.0                                                         | 3.7                  | 15.3                      | 15.8                | 1.5       |
| CO          | 2057.7–2058.0, 2069.56–2069.76, 2137.9–2159.15                                     | 1.7                  | 2.4                       | 3.0                 | 2.2       |
| H₂CO        | 2763.425–2763.60, 2765.725–2765.975, 2778.15–2779.1, 2780.65–2782.0               | 8.4                  | 12.7                      | 16.5                | 1.2       |
| HCl         | 2727.73–2727.83, 2775.7–2775.8, 2925.8–2926.0                                     | 1.6                  | 2.0                       | 2.7                 | 1.8       |
| HCN         | 3268.05–3268.4, 3287.1–3287.35, 3299.3–3299.6, 3331.4–3331.8                      | 5.1                  | 3.9                       | 6.5                 | 2.2       |
| HCOOH       | 1102.0–1109.0, 1178.4–1178.8                                                      | 9.4                  | 10.7                      | 16.2                | 1.1       |
| HF          | 4038.86–4039.05                                                                    | 1.9                  | 2.3                       | 3.3                 | 1.9       |
| HNO₃        | 867.6–870.0                                                                        | 3.4                  | 0.4                       | 3.4                 | 1.3       |
| N₂O         | 2481.2–2482.6, 2526.4–2528.2, 2537.85–2538.8, 2540.1–2540.7                      | 1.5                  | 3.6                       | 4.0                 | 3.0       |
| NH₃         | 930.32–931.32, 966.97–967.675                                                     | 13.1                 | 11.8                      | 19.0                | 1.1       |
| O₃          | 782.56–782.86, 788.85–789.37, 993.3–993.8, 1000.0–1004.5                          | 1.5                  | 5.3                       | 5.5                 | 4.4       |

2.2. Retrievals

The solar absorption spectra recorded by the DA8 were processed using the SFIT4 retrieval algorithm (https://wiki.ucar.edu/display/sfit4/). SFIT4 uses the optimal estimation method (OEM, Rodgers 2000), and works by iteratively adjusting the target species volume mixing ratio (VMR) profile until the difference between the calculated spectrum and the measured spectrum meets the convergence criterion. The retrieval uses spectroscopic parameters from HITRAN 2008 (Rothman et al 2009), and atmospheric information (temperature and pressure profiles for any particular day) provided by the US National Centers for Environmental Prediction (NCEP). C₂H₄, CH₄, CO, HCl, HCN, HF, HNO₃, N₂O, and O₃ are standard NDACC IRWG products, and were retrieved using harmonized microwindows and a priori VMR profiles following methods described by Lutsch et al (2020) and references therein. The spectral fitting microwindows for each species are listed in table 1. The a priori profiles were obtained by averaging Whole-Atmosphere Community Climate Model (WACCM V4) profiles from 1980 to 2020 (40-year average) (Eyring et al 2007, Marsh et al 2013). Other gases measured at TAO are not standard NDACC species, but are archived there as well (CH₃OH, H₂CO, HCOOH and NH₃). CH₄, CO and O₃ are also contributed to the Copernicus Atmospheric Monitoring Service (CAMS) Rapid Delivery system (https://atmosphere.copernicus.eu/).

Uncertainties in the retrievals include forward model errors, measurement noise, and smoothing errors that arise due to the discretized vertical resolution. Forward model errors include temperature, pressure, line width, line strength, and solar zenith angle uncertainties, while measurement noise error include errors due to uncertainties in instrument line shape, interfering species, and wavelength shifts. Error analysis was performed on all retrievals (following Rodgers (2000)), grouped into random and systematic uncertainties, and added in quadrature. The resulting mean uncertainties on the retrieved species, averaged over the entire time series, are listed in table 1. Degrees of freedom for signal (DOFS), the trace of the averaging kernels used in the retrievals, can be used to determine how much vertical information the retrieval contains (e.g., Vigouroux et al 2009). The DOFS for each species averaged over the time series are also listed in table 1.
2.3. Model
The GEOS-Chem (v.12.1.1) CTM tagged CO simulation (The International GEOS-Chem User Community 2018) was used to identify major sources of CO over Toronto. This simulation was conducted at $2^\circ \times 2.5^\circ$ resolution using MERRA-2 (Modern-Era Retrospective analysis for Research and Applications, Version 2) meteorological fields (Molod et al. 2015) and the GFAS (Global Fire Assimilation System) biomass burning emissions database (Kaiser et al. 2012). The tagged run uses prescribed monthly mean OH fields to account for the chemical loss of CO, which allows for the use of separate tracers to track CO from different sources, including biomass burning emissions from specific regions, CO produced from CH$_4$ oxidation (Fisher et al. 2017) and anthropogenic emissions (e.g., Whaley et al. 2015, Yamanouchi et al. 2020a). The model was run from 2002 to 2018, and model output from 2003 and onwards was used for analysis (one year for spin-up). Further details of the GEOS-Chem tagged CO simulation can be found in Lutsch et al. (2020).

The GEOS-Chem (v.12.3.2) tagged CH$_4$ simulation was used to estimate sources of CH$_4$ over Toronto. The model was previously used by Bader et al. (2017) to assess contributions to increased CH$_4$ over NDACC FTIR stations. In this study, the model was run at $2^\circ \times 2.5^\circ$ resolution using MERRA-2 meteorological fields. This model is able to trace back CH$_4$ emitted from sources, including oil, gas and coal mining operations, wetlands, livestock, and other anthropogenic sources. EDGAR v4.3.2 (Janssens-Maenhout et al. 2019) and Environmental Protection Agency (EPA) (Maasakkers et al. 2016) emissions databases were used, and the oil, gas and coal mining emission inventories of CH$_4$ over Canada and Mexico were taken from Sheng et al. (2017). QFEDv2.4r8 inventory (https://gmao.gsfc.nasa.gov/pubs/docs/Darmenov796.pdf) was used for biomass burning emissions. Recent studies (e.g., Baray et al. 2018) have shown that Canadian oil-sands emissions may be higher than expected, and thus may result in the model underestimating the oil and gas contributions to CH$_4$ over Toronto. In fact, Baray et al. (2018) have shown, through aircraft measurements taken in summer 2013, that CH$_4$ emissions from the Athabasca Oil Sands Region were 48% ± 8% higher than the values in the 2013 Canadian Greenhouse Gas Reporting Program inventory. Due to these issues, the model was not used in this study to attribute drivers of trends seen in the FTIR data, only to estimate sources of CH$_4$ over Toronto. Model data from 2002 to 2018 were used for this study. The model was spun-up for 25 years, then subsequently spun-up again from 1992, resulting in an “effective” spin-up period of over 35 years. The longer spin-up period is required for CH$_4$ (compared to CO) due to the much longer lifetime of CH$_4$ (Bader et al. 2017).

2.4. Trend analysis and identification of enhancement events
With measurements spanning 18 years, long-term trends of TAO FTIR columns can be examined. While a trend analysis using monthly averages is possible (e.g., Angelbratt et al. 2011a), this study fitted Fourier series of several orders (Weatherhead et al. 1998). It should be noted that the FTIR measurements have systematic (non-random) errors (see table 1); to address this, bootstrap resampling was utilized to derive the confidence interval of the trends. Bootstrap resampling allows for a robust treatment of non-normally distributed dataset (Gatz and Smith 1995), and provides a methodology for assessing the confidence intervals on trends of atmospheric data (Gardiner et al. 2008). In this study, resampling was done with a Q value (the number of bootstrap resampling ensemble members generated for statistical analysis) of 5000 (following Gardiner et al. 2008). All of these techniques were combined to assess the intra- and inter-annual trends of the trace gases measured at TAO.

The Fourier fit was also used to identify enhancement events, following Zellweger et al. 2009. This analysis is done by taking the negative residuals of the fit (i.e., when measurements are smaller than the fitted values), mirroring them, and calculating the standard deviation ($\sigma$) of the mirrored residuals. Any measurements that are 2$\sigma$ above the fit are considered enhancement events. This analysis eliminates biases in the spread due to enhancement events by mirroring the negative residuals. The trend analysis and error analysis were performed twice: once on the full dataset and once on the filtered dataset to obtain the trend with enhancement events removed (see table 2). In this study, Fourier series of order 3 were utilized for all analyses. An analysis was done by comparing Fourier series fits of order 1 to 7, and checking for overfitting by running the residuals of the fit through a Kolmogorov-Smirnov normality test (Ghasemi and Zahediasl 2012). While overfitting was not observed at higher orders, they did not give more statistically-significant trends, so order 3 was chosen.

3. Results and discussion
The time series of gases measured at TAO are shown in figure 1, along with their fitted trend lines and enhancement events. Trends (in annual percentage) for each of the gases are compiled in table 2. The uncertainties (2$\sigma$) were obtained using bootstrap resampling. All analyses were done using total columns, with the only exception being O$_3$. Because O$_3$ had a mean DOFS of 4.4 (see table 1), tropospheric (0–12 km) and stratospheric (12–50 km) columns were analyzed separately (following Vigouroux et al. 2015). For C$_2$H$_6$ and
the positive trend in atmospheric CH$_4$ from 2013 to 2015 was not compatible with the mitigation required in the

CH$_4$ over TAO from 2002 to 2008 was found to have a positive trend of 0.26/%/year, with two disjointed trends, for 2002–2008 and 2009–2019, were fitted (following Franco et al 2016a). GEOS-Chem tagged runs of CH$_4$ and CO are shown in figures 2(a) and 2(b), respectively.

### 3.1. CH$_4$

CH$_4$ over TAO from 2002 to 2008 was found to have a positive trend of 0.26 ± 0.10 and 0.24 ± 0.07%/year, with and without enhancement events respectively (see figure 1(c)). These values are consistent with findings from Angelbratt et al (2011a), where analysis of European (Jungfraujoch (46.6°N, 8.0°E), Kiruna (67.8°N, 20.4°E) and Zugspitze (47.4°N, 11.0°E)) FTIR data from 1996 to 2007 yielded linear trends ranging from 0.13 ± 0.01 to 0.25 ± 0.02%/year. In the subsequent years (2009 to 2019), the TAO trend increased to 0.41 ± 0.03%/year and 0.38 ± 0.02%/year, with and without enhancement events, respectively. The slightly smaller trend after the removal of enhancement events suggests that enhancement events are becoming more frequent. Saunois et al (2016), using assimilated global CH$_4$ surface concentration data (Masarie 1994), found that the increasing rate of the positive trend in atmospheric CH$_4$ from 2013 to 2015 was not compatible with the mitigation required in the Representative Concentration Pathways of 2.5, 4, and 6 W m$^{-2}$ (for reference, the dataset used by Saunois et al (2016) for 2018 estimates an annual concentration of 1857.28 ± 0.81 ppb and an increase of 8.82 ± 0.49 ppb (https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/)).

The tagged GEOS-Chem run shows the largest contributor to CH$_4$ over TAO to be wetland emissions, which contributed 31.7 ± 0.5% of the CH$_4$ column, averaged from 2002 to 2018. Oil, gas and coal mining emissions accounted for 20.4 ± 0.3% of CH$_4$. Oil and gas alone accounted for 14.9 ± 0.2%, and coal, 5.5 ± 0.1%. Livestock emissions also accounted for a significant portion of CH$_4$, at 20.1 ± 0.2%. Contributions from other anthropogenic sources were smaller, at 4.0 ± 0.1%/year (see figure 2(a)). This may in part be due to the coarse resolution of the model (at 2° × 2.5°, the grid box is roughly 220 km by 200 km). The grid box containing TAO (and by extension downtown Toronto) also contains areas west of the city that have high livestock emissions, as estimated by the EDGAR emissions database. However, without further analysis (e.g., tagging emissions by geographical regions), it is unclear to what extent the local emissions are contributing to the CH$_4$ total columns in this grid cell, especially given the relatively long lifetime of CH$_4$. Additionally, as noted in section 2.3, recent studies have shown CH$_4$ emissions from the Canadian oil sands region to be underestimated. Updated emissions databases are needed for reliable estimates of emissions contribution to CH$_4$ over TAO and elsewhere (e.g., Mostafavi Pak et al 2019).
Figure 1. Time series and fitted trends of TAO total columns of (a) C$_2$H$_2$, (b) C$_2$H$_6$, (c) CH$_4$, (d) CH$_3$OH, (e) CO, (f) H$_2$CO, (g) HCl, (h) HCN, (i) HCOOH, (j) HF, (k) HNO$_3$, (l) N$_2$O, (m) NH$_3$, (n) tropospheric (0 to 12 km) column of O$_3$, and (o) stratospheric (12 to 50 km) column of O$_3$. For (b) C$_2$H$_6$ and (c) CH$_4$, separate fits were done for data before and after 2009. The gap in the CH$_4$ time series is due to instrumental issues, which affected CH$_4$ data in particular.
3.2. C\textsubscript{2}H\textsubscript{6}

C\textsubscript{2}H\textsubscript{6} was found to be decreasing from 2002 to 2008, at rates of −0.74 ± 0.73 and −1.31 ± 0.61%/year, with and without enhancement events, respectively (see figure 1(b)). This is in agreement with trends observed in Harestua (60.2°N, 10.8°E) and Kiruna from 1996 to 2006, at −1.09 ± 0.25 and −1.14 ± 0.18%/year, respectively (Angelbratt et al. 2011b). The trends for the subsequent years (2009 to 2019) were reversed, with increasing trends of 1.19 ± 0.27 and 0.94% ± 0.20%/year, with and without enhancement events respectively. Bootstrap resampling error analysis shows these trends to be significant (i.e., the 2σerror bars do not overlap 0%). The recent C\textsubscript{2}H\textsubscript{6} trend retrieved in this analysis is lower than estimates given by Franco et al. (2016a), where growth rates of 3%−5%/year were seen when analyzing FTIR datasets from 2009 to 2014 from Eureka (80.1°N, 86.4°W), Thule (76.5°N, 68.8°W), TAO, Boulder (40.4°N, 102.5°W), and Mauna Loa (19.5°N, 155.6°W). For reference, the methodology used in this study yielded a trend of 5.17 ± 0.68%/year using 2009-2014 data, and 0.30 ± 0.79%/year for 2015-2019.

3.3. CO

CO over TAO exhibited a decreasing trend (see figure 1(e)), at an annual rate of −0.90 ± 0.07% (−0.87 ± 0.05%/year after removal of enhancement events). This is in agreement with the CO trend seen in Zugspitze (1996 to 2006), which was observed to be −1.00 ± 0.24%/year (Angelbratt et al. 2011b). This result is also comparable to values seen at Lauder, New Zealand (45°S, 170°E), and at Arrival Heights, Antarctica (78°S, 167°E), both from 1997 to 2009, where annual trends of −0.94 ± 0.47 and −0.92 ± 0.46%/year were observed, respectively (Zeng et al. 2012).

The GEOS-Chem tagged CO simulation shows CH\textsubscript{4} oxidation to be a major source of CO over Toronto, accounting for 30.9 ± 4.4% of CO in the grid containing TAO, averaged over 2003 to 2018. North American fossil fuel emissions accounted for 13.9 ± 4.0%, while Asian fossil fuel sources accounted for 16.8 ± 5.3%. All other anthropogenic sources contributed 4.7 ± 1.3% (see figure 2(b)). CO over Toronto from North American and European fossil fuel sources exhibited a decreasing trend of −2.64 ± 0.18 and −1.63 ± 0.14%/year, respectively, while Asian fossil fuel sources showed an increasing trend of 0.37 ± 0.08%/year. North American biomass burning sources also showed an increasing trend, at a rate of 1.56 ± 0.47%/year. Trends and their errors were obtained using the same methodology as the FTIR data. Fossil fuel contributions exhibit seasonality, peaking in the winter months. North American biomass burning contributed 3.6 ± 3.4%, although values as high as 39.8% were seen in 2015, during a biomass enhancement event (Yamanouchi et al. 2020a).

3.4. N\textsubscript{2}O

The time series of TAO N\textsubscript{2}O (see figure 1(l)) shows a steady and statistically robust trend, increasing at a rate of 0.28 ± 0.02%/year (0.26 ± 0.02%/year without enhancement events). This is similar to findings from other FTIRs, such as 0.21 ± 0.01, 0.19 ± 0.01, 0.40 ± 0.02, and 0.29 ± 0.02%/year at Jungfraujoch, Zugspitze,
Harestua, and Kiruna, respectively from 1996 to 2007 (Angelbratt et al. 2011a), as well as an estimate from surface observations given by IPCC (2007) of 0.26%/year. This is also comparable to the global trend estimates obtained from satellite-borne instruments, such as 0.22%/year from AIRS (trend estimated using data from 2003–2013, at 200–750 hPa) (Xiong et al. 2014), as well as 0.2559 ± 0.0080%/year from ACE–FTS (using data from 2004–2020, at 60°S to 60°N, 5.5 to 10.5 km in altitude) (Bernath et al. 2020).

3.5. \( \text{O}_3 \)

Tropospheric and stratospheric time series of \( \text{O}_3 \) can be seen in figures 1(n) and 1(o), respectively. TAO \( \text{O}_3 \) exhibits a seasonal cycle with a peak in February for both regions of the atmosphere. This can be contrasted with lower troposphere and surface \( \text{O}_3 \) in Toronto, which peak in April–June and July, respectively (Whaley et al. 2015).

TAO tropospheric \( \text{O}_3 \) showed an increasing trend of 0.28 ± 0.19%/year (0.41 ± 0.15%/year without enhancement events). Stratospheric \( \text{O}_3 \) did not exhibit a significant trend. The increasing tropospheric \( \text{O}_3 \) trend seen in Toronto can be contrasted to findings by Vigouroux et al. (2015), where tropospheric \( \text{O}_3 \) trends at Harestua, Ny–lesund (78.9°N, 11.9°E) and Thule were observed to be −3.1 ± 0.20%/decade, −5.8 ± 3.2%/decade and −5.3 ± 4.4%/decade, respectively. These trends were observed with FTIR measurements from 1995 to 2012 (Harestua and Ny–lesund), and 1999 to 2012 (Thule). This may be due to differences in sources, given the urban location of TAO compared to these remote Arctic sites. Gaudel et al. (2018) found no consistent trend in tropospheric ozone ozone anomalies derived from time series at eight FTIR stations. Whaley et al. (2015) have shown that TAO \( \text{O}_3 \) is highly sensitive to fossil fuel emissions of \( \text{NO}_x \).

3.6. Other Species

Total columns of other gases measured at TAO exhibited statistically robust trends. The exception was \( \text{CH}_3\text{OH} \), which showed no significant trends (at the 2\( \sigma \) confidence interval), with or without enhancements. This is in agreement with findings by Bernath et al. (2020), who found no significant trends in \( \text{CH}_3\text{OH} \) using global ACE–FTS data. \( \text{C}_2\text{H}_2 \) exhibited (see figure 1(a)) a decreasing trend at a rate of −1.12 ± 0.30%/year (−1.21 ± 0.26%/year without enhancement events), also comparable to −1.29 ± 0.38%/year given by Bernath et al. (2020). \( \text{HCOOH} \) showed a decreasing trend of −2.15 ± 0.64%/year, but after removing enhancement events, the trend was found to be −0.73 ± 0.53%/year. This is a greater rate of decrease in \( \text{HCOOH} \) than the global trend estimate of −0.51 ± 0.28%/year obtained from ACE–FTS (Bernath et al. 2020). HCN also showed a decreasing trend of −0.51 ± 0.21%/year, comparable with −0.93 ± 0.47%/year seen at Lauder (Zeng et al. 2012). \( \text{H}_2\text{CO} \) showed a statistically significant trend only after removing enhancements (−0.43 ± 0.25%/year). Another FTIR study by Lieschke et al. (2019) also observed a negative \( \text{H}_2\text{CO} \) trend using an FTIR at Wollongong (34.41°S, 150.88°E), but with a larger magnitude, at −1.9%/year (2\( \sigma \) confidence interval at −2.2 to −1.7) using data from 1996 to 2015. These can be contrasted with the value calculated by Franco et al. (2016) of 0.81 ± 0.62%/year, which was obtained by analyzing FTIR data from 2003 to 2015 at Jungfraujoch, a high-altitude location. \( \text{NH}_3 \) was found to be increasing at 3.56 ± 0.85%/year (2.36 ± 0.57%/year without enhancement events), comparable to 2.61%/year obtained from AIRS satellite measurements over the USA (Warner et al. 2017).

Several stratospheric species exhibited statistically significant trends. For HF, the trend was 0.59 ± 0.11%/year (and 0.47 ± 0.09%/year after removing enhancement events) (see figure 1(j)). A previous analysis FTIR HF by Kohlhepp et al. (2012) obtained annual trends of 0.61 ± 0.70%, −0.04 ± 0.61%, 1.07 ± 0.28% and 0.68 ± 0.58%, over Ny–lesund, TAO, Lauder and Arrival Heights, respectively, using data from 2000 to 2009 (2002 to 2009 for TAO; using our methodology yields −0.19 ± 0.41%/year for this period). The HF trend over Toronto can also be contrasted with ACE–FTS observations, which saw a trend of 0.864 ± 0.047%/year (from 2004 to 2020) averaged over the globe (Bernath et al. 2020). Kohlhepp et al. (2012) has suggested that, because fluorine emission is not explicitly restricted, HF total columns are expected to keep increasing.

HCl showed a decreasing trend of −0.11 ± 0.04%/year (and −0.07 ± 0.06%/year after removing enhancement events). This is a smaller magnitude negative trend compared to a previous analysis of TAO HCl by (Kohlhepp et al. 2012), who observed −1.22 ± 0.37%/year when examining data from 2002 to 2009 (our methodology yields −1.36 ± 0.33%/year for this period). \( \text{HNO}_3 \) was found to be increasing at 0.36 ± 0.13%/year, or 0.43 ± 0.12%/year after removing enhancement events (see figure 1(k)). This is lower than (although within combined errors of) the global trend from ACE–FTS of 0.60 ± 0.17%/year (Bernath et al. 2020), and can be contrasted with older FTIR studies, which found no significant trends of \( \text{HNO}_3 \) (e.g., Rinsland et al. 1991).

4. Conclusions

The FTIR spectrometer situated at TAO in downtown Toronto, Ontario, Canada has been operational since mid-2002, and in this study, the 18-year time series (2002–2019) of total columns of \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_6 \), \( \text{CH}_4 \), \( \text{CH}_3\text{OH} \),
CO, H2CO, HCl, HCN, HCOOH, HF, HNO3, N2O, NH3 and O3 were presented, and their trends analyzed. This is the first time that long-term trends of CH3, HCN, HNO3, N2O, the stratospheric and tropospheric O3 over Toronto from an FTIR have been presented.

TAO CH4 was seen to have an upward trend of 0.41 ± 0.03%/year and 0.38 ± 0.02%/year after 2009, with and without enhancement events, compared to 0.26 ± 0.10%/year (0.24 ± 0.07%/year after removing enhancement events) for 2002 to 2008. The GEOS-Chem tagged CH4 run shows that the largest contributor to CH4 over Toronto to be wetland emissions, with an average relative contribution of 31.7 ± 0.5%. A similar analysis of CH3 showed a decreasing trend from 2002 to 2008, at a rate of −0.74 ± 0.73 (−1.31 ± 0.61%/year without enhancement events), followed by an increasing trend of 1.19 ± 0.27%/year (no enhancement data: 0.94 ± 0.20%/year) from 2009 to 2019.

TAO CO was found to be decreasing at a rate of −0.90 ± 0.07%/year. The tagged CO GEOS-Chem simulation showed that contributions from Asian fossil fuel sources increased, while that from North America decreased, at rates of 0.37 ± 0.08 and −2.64 ± 0.18%/year, respectively. North American biomass burning contributions showed an increasing trend of 1.56 ± 0.47%/year. N2O over TAO also showed a robust trend, increasing at 0.28 ± 0.02%/year (0.26 ± 0.02%/year without enhancement events). Tropospheric O3 columns (0–12 km) exhibited a trend of 0.28 ± 0.19%/year (0.41 ± 0.15%/year without enhancement events), while the stratospheric column (12–50 km) showed little to no statistically significant trend (−0.05 ± 0.07%/year).

Bootstrap reanalysis resulted in statistically robust trends for most species retrieved at TAO, with the exception of CH3OH and H2CO.

Continued atmospheric monitoring is essential for understanding the trends and variability of atmospheric compositions, as well as for evaluating the impact of emissions from wildfires, and anthropogenic activities such as oil and gas production. This information is necessary not only for advancing our understanding of atmospheric science, but also for decision-makers who require scientific data and some level of predictive capability to make meaningful decisions on policies regarding topics such as climate change and air pollution. FTIR measurements over 18 years enabled the determination of trends for 14 species, including stratospheric species, tropospheric pollutants, and greenhouse gases.

Acknowledgments

The TAO FTIR data are available from the NDACC data portal at [http://www.ndaccdemo.org/stations/toronto-canada](http://www.ndaccdemo.org/stations/toronto-canada). The GEOS-Chem model (v12.1.1 and v12.3.2) is freely available to the public [The International GEOS-Chem User Community](https://www.geos-chem.org). Instructions for downloading and running the models can be found at [http://wiki.seas.harvard.edu/geos-chem/index.php/Getting_STARTED_with_GEOS-Chem](http://wiki.seas.harvard.edu/geos-chem/index.php/Getting_STARTED_with_GEOS-Chem). Information about the GEOS-Chem model and the configurations used in this study are described in text. This work, including measurements made at TAO, was supported by Environment and Climate Change Canada, the Natural Sciences and Engineering Research Council of Canada (NSERC) and the NSERC CREATE Training Program in Technologies for Exo-Planetary Science. We would like to thank the many students and post-doctoral fellows who have been involved in making measurements at TAO, particularly Aldona Wiacek, Jeff Taylor, and Cyndi Whaley.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: [https://www.ndaccdemo.org/](https://www.ndaccdemo.org/).

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