Using FTIR-Spectroscopy to Measure Atmospheric Trace Gas Concentrations Over Toronto

Shoma Yamanouchi, Kimberly Strong

Department of Physics, University of Toronto

NDACC IRWG & TCCON Meeting
11 - 15 June 2018
Mexico

U of Toronto Atmospheric Observatory (TAO)

Location:
43.66N, 79.40W,
174 masl

↓ Solar tracker

- Primary instrument:
  - ABB Bomem DA8 Fourier transform infrared (FTIR) spectrometer
- Measurements started in 2002
- Urban site (downtown Toronto)

Scientific Objectives

- To assess biomass burning emissions and quantify its emission factors
- To investigate the daily, seasonal, and interannual trace gas variability and trends in an urban setting (downtown Toronto)
- To characterize the origin of urban pollution events (local or long-range transport) with models (e.g., the GEOS-Chem chemical transport model)

Biomass Burning

- Biomass burning emissions can negatively affect air quality
- Emissions can have photochemical and radiative forcing effects, particularly when plumes are transported to Arctic regions (Amiro et al., 2001)
- Quantifying biomass burning emissions and understanding their transport poses a challenge
  - Types of vegetation burned, the combustion phase (smoldering vs. flaming), and atmospheric conditions at the time of the fire must all be accounted for when quantifying emissions
  - Emitted gases may also undergo chemistry in the atmosphere during transport, which must be accounted for

Biomass Burning Enhancement Events

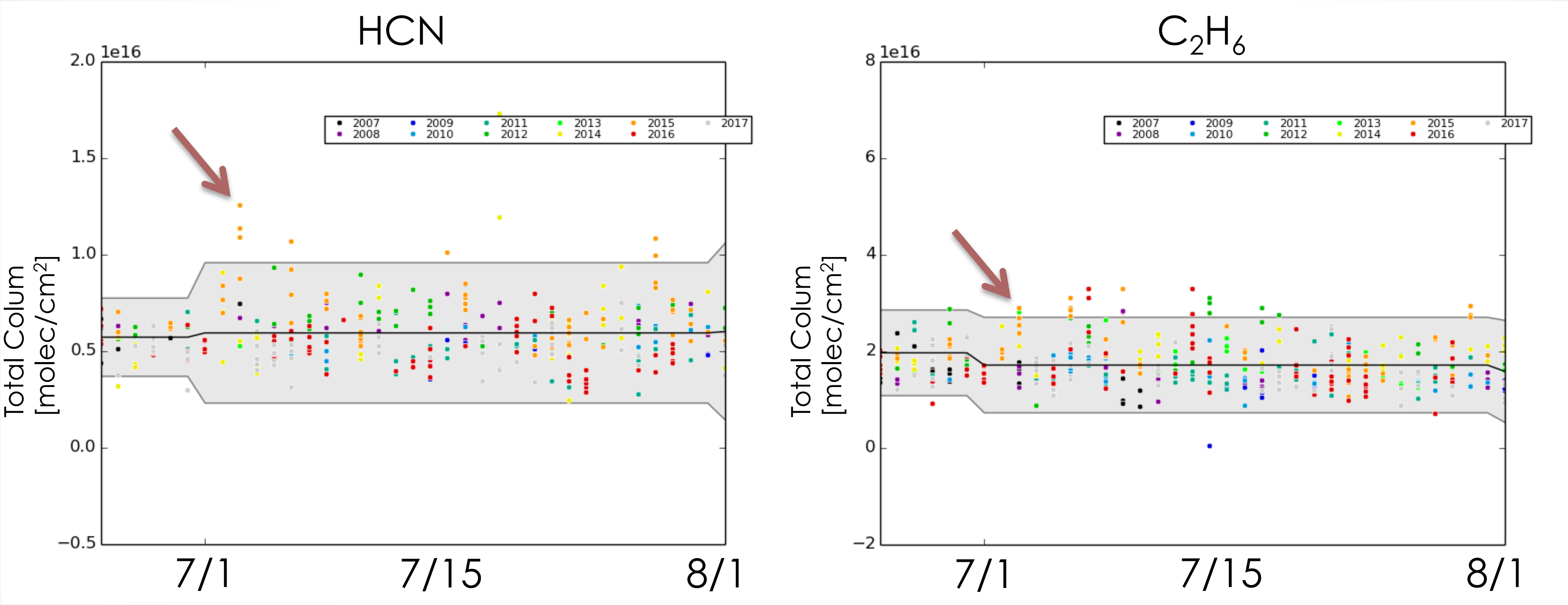
- Wildfires emit numerous chemical species including CO, C_2H_6, HCN, HCOOH, H_2CO, C_2H_2 and others
- Given their long lifetimes, CO, HCN and C_2H_6 are good tracers of biomass burning events (e.g., Viatte et al., 2013)
- Formic acid and formaldehyde have shorter lifetimes
  - Typical lifetimes (τ) are: 61 days (CO), 45 days (C_2H_6), 150 days (HCN), ~4 days (HCOOH) and ~1 day (H_2CO) (Viatte et al., 2013, Millet et al., 2015, Pommier et al., 2017)

Biomass Burning Analysis

- Analyzing the 2015 early July biomass burning enhancement event observed at TAO
  - Simultaneous enhancements of HCN, CO, C_2H_6 and HCOOH
  - HCOOH is an important gas in the atmosphere as it greatly contributes to free precipitation acidity
- FLEXPART used for source attribution
- Travel-time estimated with HYSPLIT
  - Travel-time used to estimate decay in the atmosphere
- Emission factors and emission ratios reported

Early July 2015

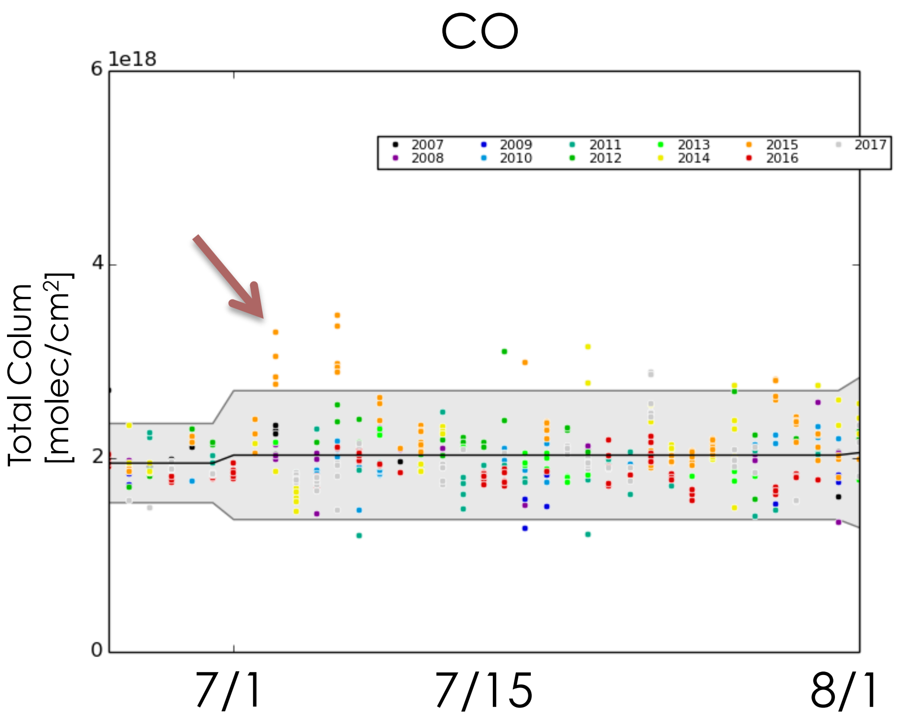
- Notice the sharp peak in HCN on July 3–6
- C_2H_6 enhancement is less obvious, likely due to C_2H_6 having local sources

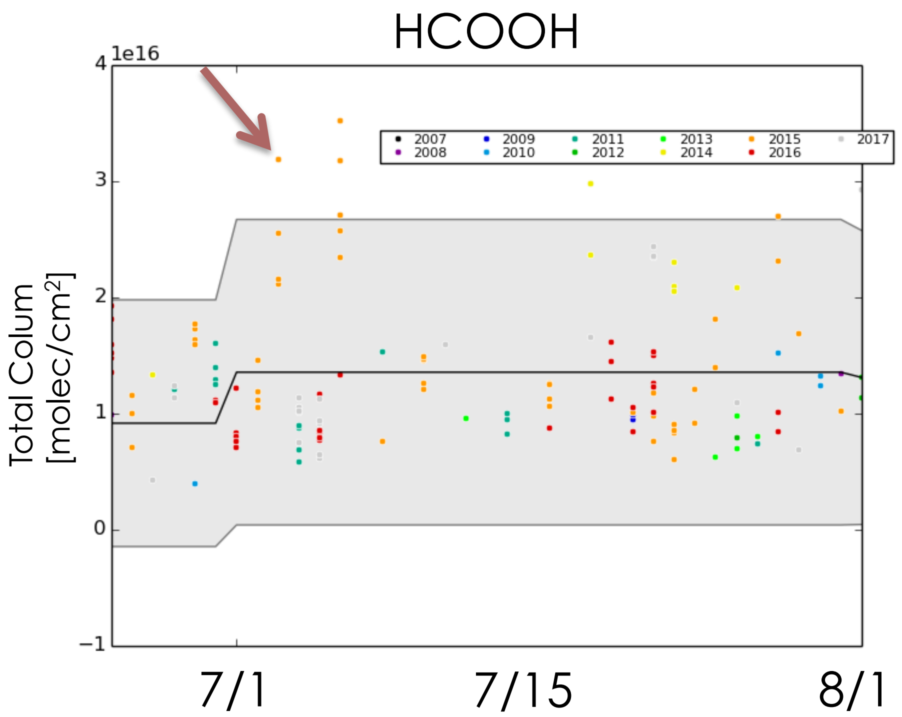


- Orange dots are 2015 data points
- Gray band indicates 2 standard deviations above and below the monthly mean

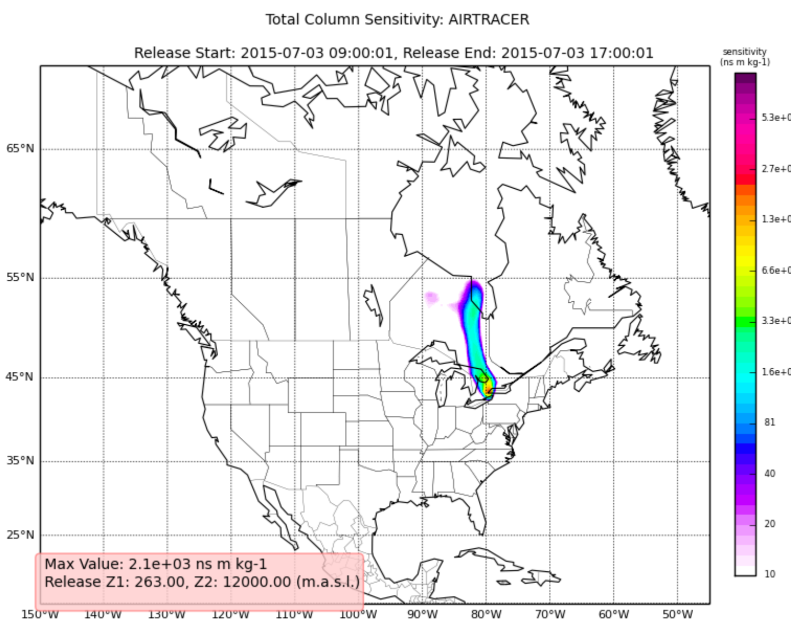
Early July 2015 Cont.

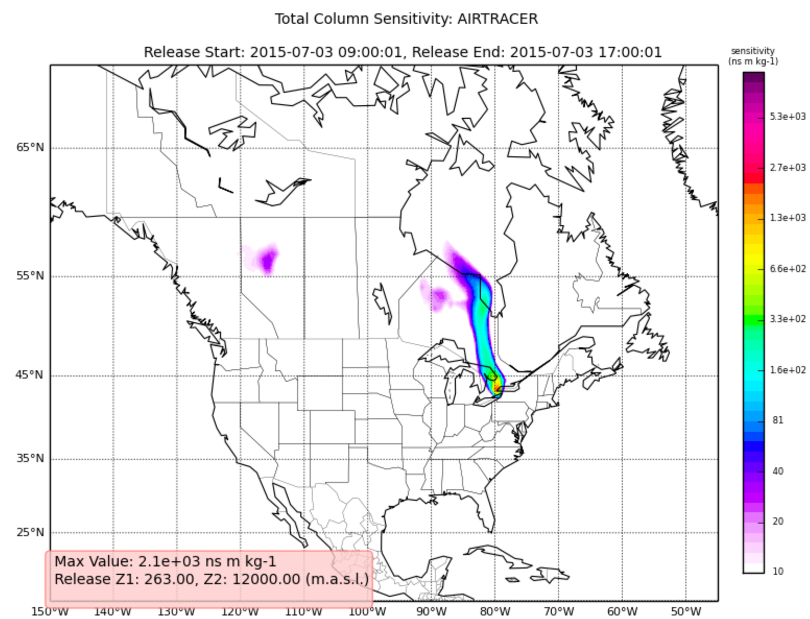
- CO is also clearly enhanced on July 3rd and 6th
- HCOOH is concurrently enhanced





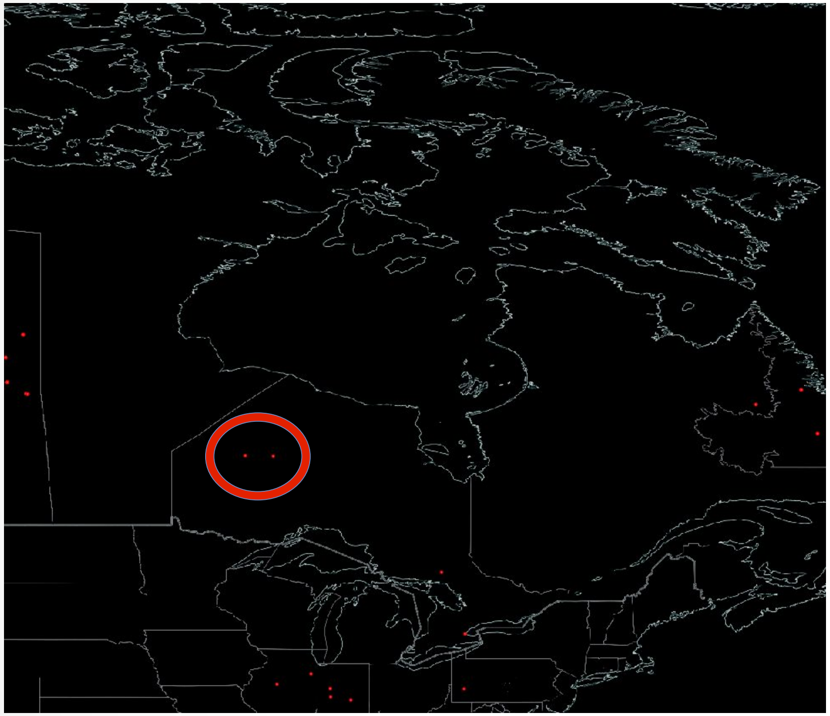
July 3rd Analysis with FLEXPART

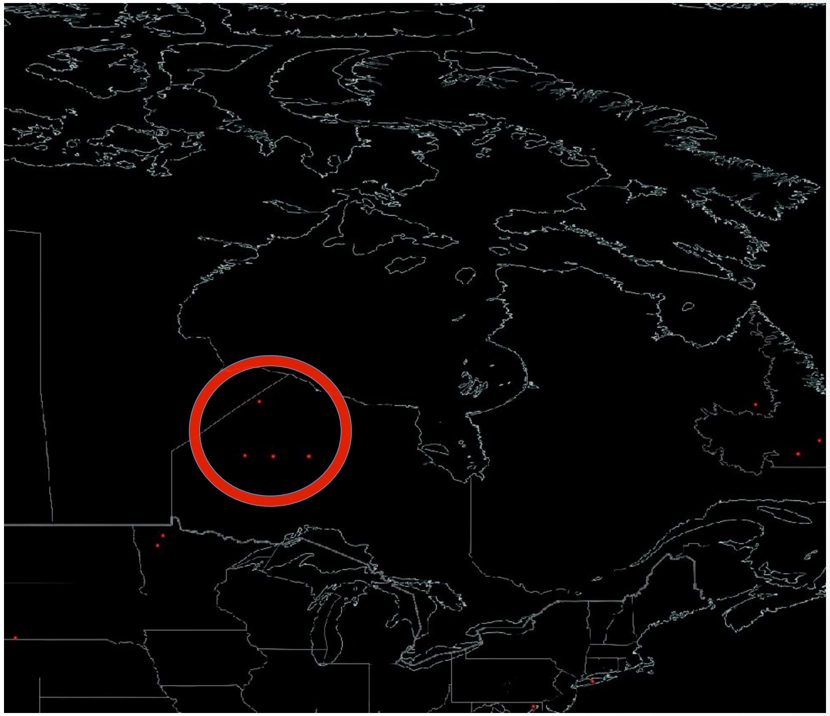




FLEXPART 2-day and 3-day back-trajectory runs (both July 3rd release), left and right respectively

Comparison with MODIS Fire Data

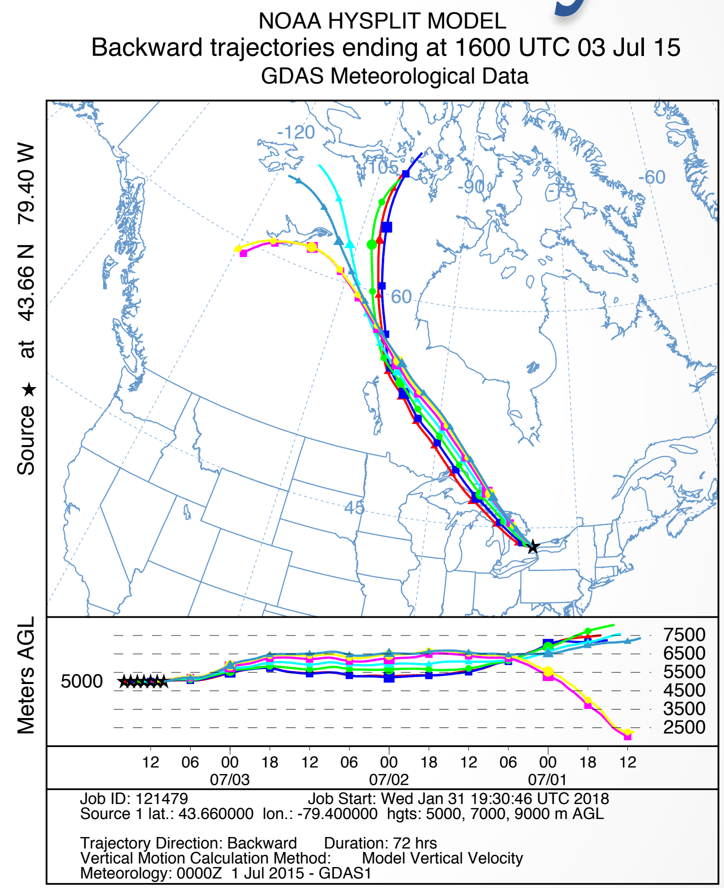




- MODIS Fire Product is an online tool for detecting fire anomalies
  - MODIS is onboard satellites TERRA and AQUA
- Fire events detected by MODIS on July 1st and 2nd, left and right respectively

Travel Time and Decay

- Chemical species decay exponentially in the atmosphere
  - i.e., $[x]_t = [x]_0 e^{-t/\tau}$
  - Where τ denotes the lifetime
- HYSPLIT back trajectory was run with GDAS meteorological field for travel time estimation
- For this event travel time was taken to be 2 days



Interpreting the Data

- Enhancement Ratio (EnhR)
  - Ratio of column of species of interest to column of CO
  - Calculated for HCN, C_2H_6 and HCOOH
  - EnhR is the slope of the linear regression when the two species are plotted against each other
  - To account for the travel time decay and to calculate the emission ratio (ER), the following equation is used:

$$ER_X = EnhR_X \left(\frac{e^{t/\tau_X}}{e^{t/\tau_{CO}}} \right)$$

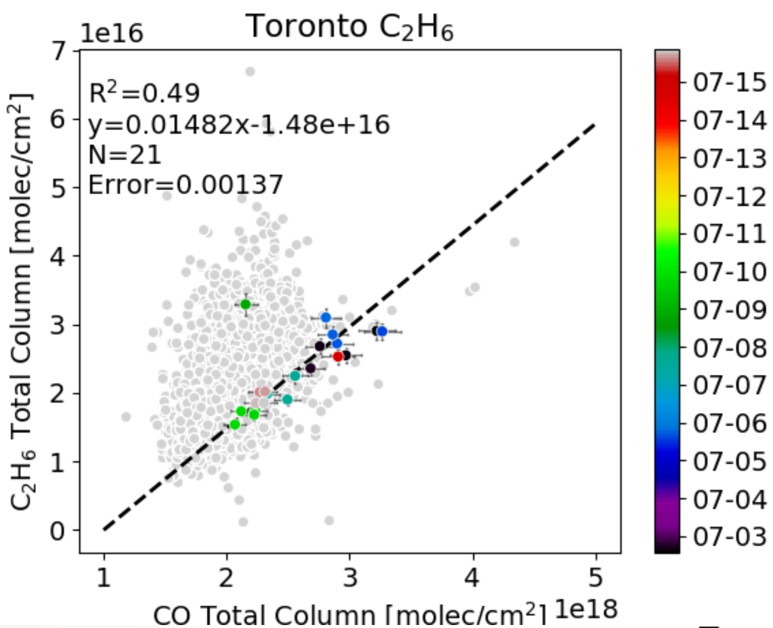
ER and EF

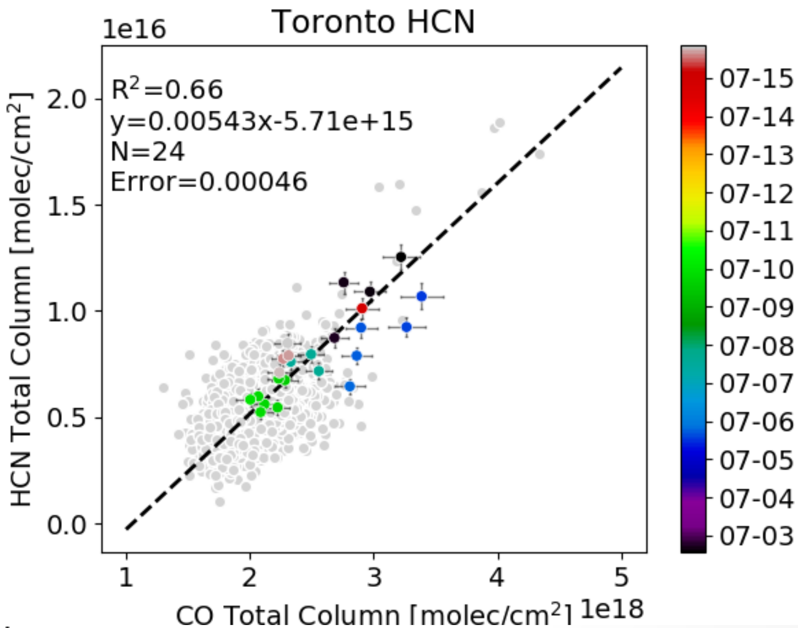
- ER: Emission Ratio
  - Enhancement ratio with plume aging correction
  - Since travel times are accounted for, it is not location specific
- EF: Emission Factor
  - Defined by:

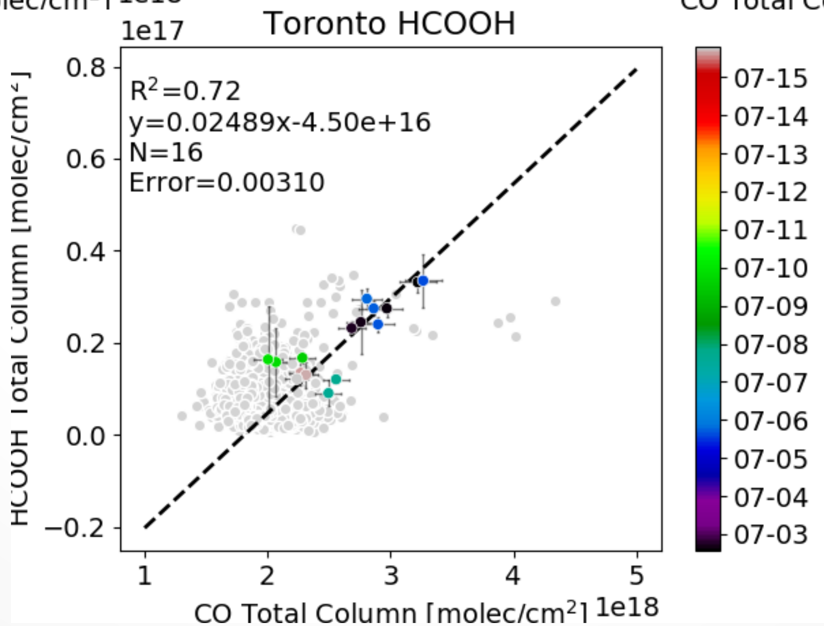
$$EF_X = EF_{CO} \cdot ER_X \cdot \left(\frac{MW_X}{MW_{CO}} \right)$$

    - where EF_{CO} is the emission factor of CO, which is 127 ± 45 g/kg (Akagi et al., 2011), and MW are the molecular weights
  - Not location specific

$EnhR_X$ Plots for HCN, C_2H_6 and HCOOH







Results

Emission ratios and emission factors from this study compared against other sources (measured with ground-based FTIRs)

	This study	Other studies using ground-based FTIRs
ER_{HCN}	0.0053 ± 0.0005	0.0054 ± 0.0022 [a]
ER_{C2H6}	0.0150 ± 0.0014	0.0108 ± 0.0036 [a]
ER_{HCOOH}	0.0241 ± 0.0033	0.01790 ± 0.00937 [b]
EF_{HCN}	0.65 ± 0.24 g/kg	0.66 ± 0.27 g/kg [a]
EF_{C2H6}	2.04 ± 0.75 g/kg	1.47 ± 0.50 g/kg [a]
EF_{HCOOH}	5.03 ± 1.9 g/kg	3.15 ± 1.46 g/kg [b]

- [a] Viatte et. al., 2013
- [b] Viatte et. al., 2015

Long-term Trend Analysis

- Trend analysis:
  - Fitting a trended Fourier series:

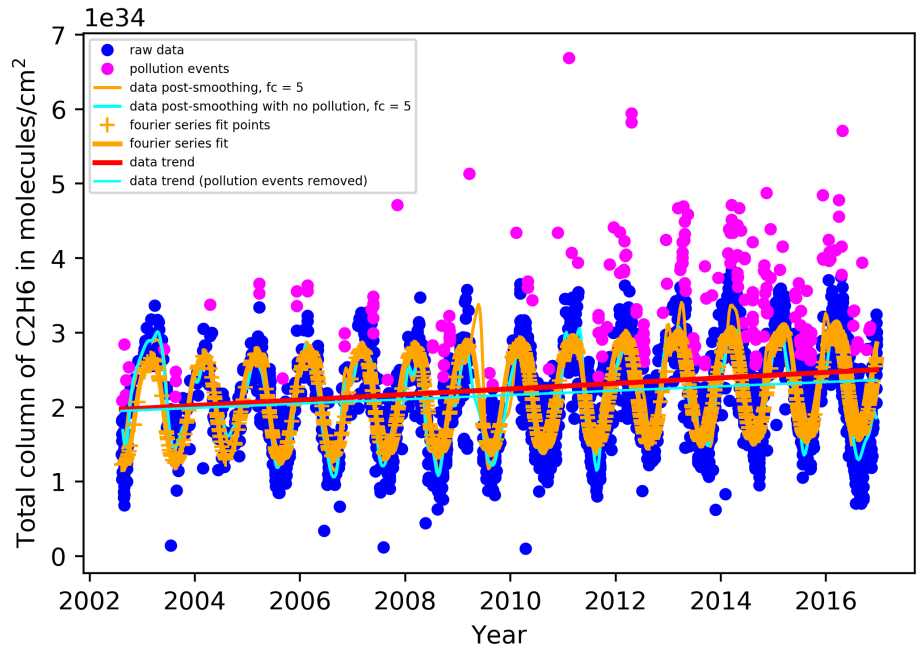
$$F(t) = a_0 + \frac{a \cdot t}{T} + \sum_{n=1}^{N} \alpha_n \sin\left(\frac{2\pi nt}{T}\right) + \beta_n \cos\left(\frac{2\pi nt}{T}\right)$$

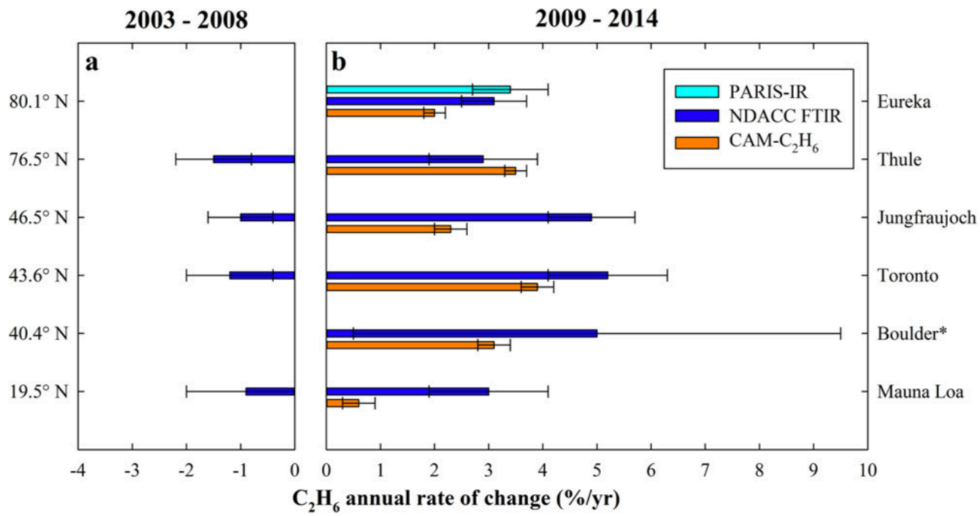
    - Where T is the total time of the data, and N is the order of the Fourier series (Taken to be 3 in this analysis)
- Pollution events are defined by:
  - Finding residuals, i.e., observation minus *F(t)*
  - Mirroring negative residuals as well as calculating the standard deviation of the residuals
  - Any measurements that are 2 standard deviations or higher than the fit and residuals are considered pollution events

(Zellweger et al., 2009 & Sandrin, 2016)

Analysis: Preliminary Results

- Top: C_2H_6 time-series data with pollution events and fitted trend-line
- According to this analysis:
  - Raw linear trend is: 1.72 ± 0.09 %
  - Linear trend with pollution removed is: 1.40 ± 0.23 %
  - The number of measurement years needed for trend detection (Weatherhead et al., 1998)
    - All data: 23.2 years
    - Pollution events removed: 24.4 years





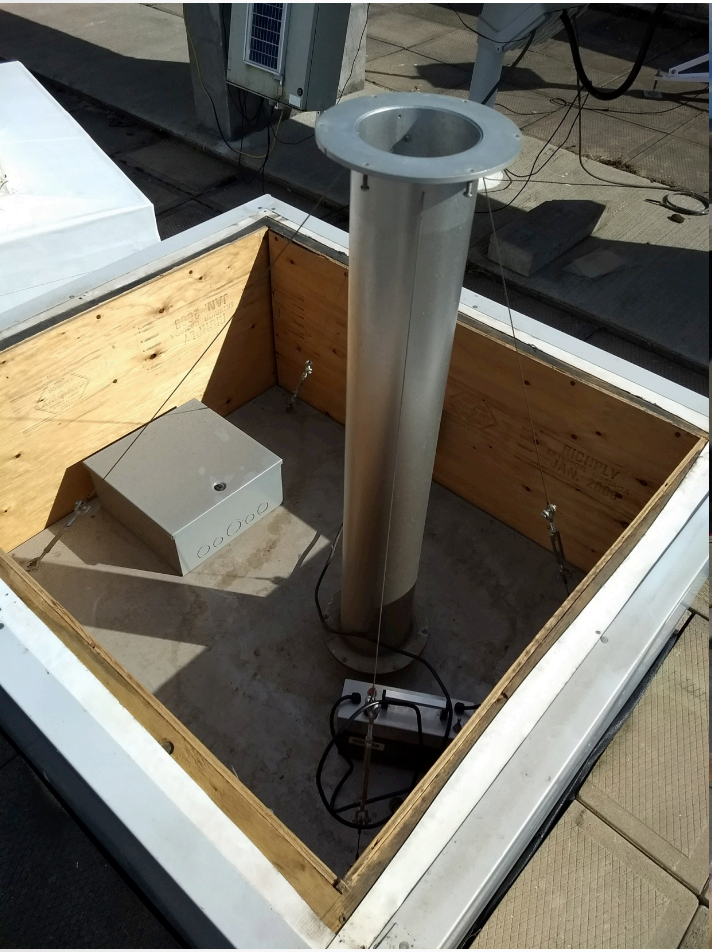
(Lower figure from Franco et al., 2016)

Future Work

- Further analysis of biomass burning plumes over Toronto
- Trend analysis of hydrocarbons and pollutants
- Analysis of pollution events with a focus on O_3 and CO
- Integration of measurements and modeling (GEOS-Chem) to assess determinants of air quality in Toronto
  - In collaboration with Dylan Jones (UofT)
- Comparison of urban (TAO) and rural (ECCC Egbert) FTIR measurements
  - Egbert is about 90 km north of downtown Toronto (TAO)
  - Egbert FTIR is in good working condition, and currently installing a new sun tracker

Egbert FTIR & Sun Tracker

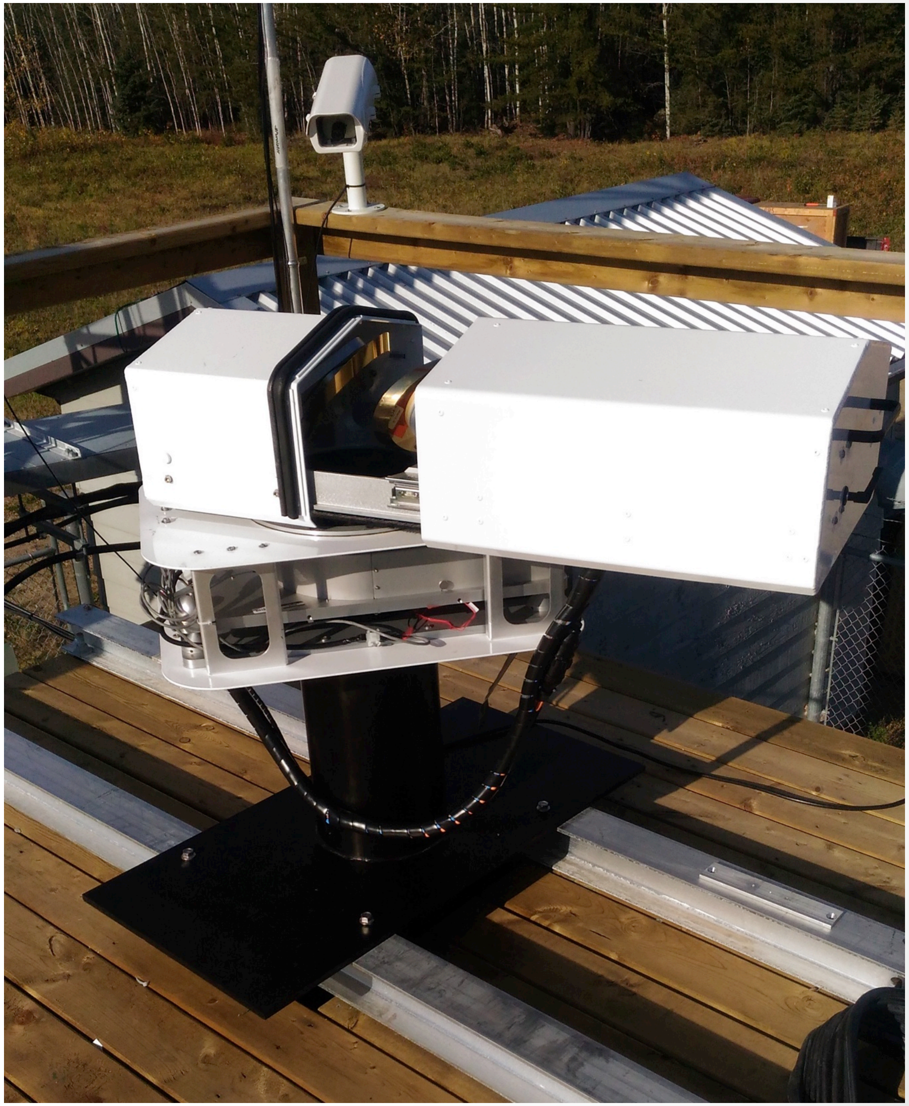
Egbert FTIR & Sun Tracker



Bruker solar tracker to be installed here

Egbert FTIR & Sun Tracker

Bruker A547 solar tracker (same model as the one to be installed at Egbert) at the East Trout Lake site



(Source: https://tccon-wiki.caltech.edu/Sites/East_Trout_Lake/Assorted_Photos/Installation_Photos)

Acknowledgements

- Technologies for Exo-Planetary Science (TEPS), NSERC
- CFI, CSA, ECCC, ORDCF, CRESTech, University of Toronto, ABB Bomem, CFCAS, PREA
- Many interns, students and postdocs who have made measurements, including : Orfeo Colebatch, Lei Liu, and Erik Lutsch

Additional Slides: Bootstrap Reanalysis

- Bootstrap resampling is done to find confidence intervals
  - It is an analysis where residuals are randomly redistributed to form a "new" set of data, where another line is refitted
  - This process is repeated (over several hundred to thousands of times)
  - The ensemble of data is analyzed to find the 2- σ confidence interval (2.5% to 97.5% coverage of the data)

(Gardiner et al., 2008)

Additional Slides: Weatherhead Method

- Detection of long-term, linear trends is affected by a number of factors
  - Size of the trend to be detected
  - Time span of the data
  - Magnitude of variability and autocorrelation
- The number of years of data needed to detect a trend strongly depends on (and increases with) the magnitude of variance and the autocorrelation coefficient
- Environmental time series data are often autocorrelated

(Weatherhead et al., 1998)

Additional Slides: More on Biomass Burning

- "As burning occurs, it can release hundreds of years worth of stored carbon dioxide into the atmosphere in a matter of hours"
  - NASA, Earth Observatory (earthobservatory.nasa.gov)
- "Exposure to biomass burning particles is strongly associated with cardiovascular disease, respiratory illness, lung cancer, asthma and low birth weights"
  - Stanford News, 2014 (news.stanford.edu)

Additional Slides: Atmospheric Formic Acid

- Formic acid is one of the most abundant acids in the atmosphere
- Greatly contributes to free precipitation acidity
- Affects aqueous phase chemistry
    - pH-dependent reaction rates
- Naturally produced photochemically, though emission sources (including anthropogenic) also certainly exist

(Millet et al., 2015)

Additional Slides: Retrieval

- A retrieval algorithm called SFIT4 is used to derive vertical profiles and/or columns of trace gases from their absorption and emission spectra:
  - Identify spectral lines of interest
  - Generate a model atmosphere using meteorology data from NCEP and WACCM
  - Use a forward model to simulate a model spectrum
  - Iteratively adjust the *a priori* VMR profile until the model spectrum agrees with the measured spectrum
- SFIT4 is an optimal estimation method (OEM) analysis
  - It uses both measurement data and the *a priori* information
  - It assigns weights to the *a priori* information and the measurement based on each of their uncertainties