Ammonia and Air Quality

Multiscale observations of NH_3 around Toronto, Canada

Shoma Yamanouchi[1], Camille Viatte[2], Kimberly Strong[1], Dylan B. A. Jones[1], Cathy Clerbaux[2], Martin Van Damme[3], Lieven Clarisse[3], and P.-F. Coheur[3]

[1]Department of Physics, University of Toronto, Toronto, Canada
[2]LATMOS - Laboratoire Atmosphères, Milieux, Observations Spatiales, Paris, France
[3]Université Libre de Bruxelles (ULB), Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), Brussels, Belgium

EGU General Assembly

May, 2020

Background

- Ammonia (NH_3) is an important pollutant
  - A major source of nitrates and fine particulate matter in the atmosphere
  - Involved in numerous biochemical exchanges affecting all ecosystems (Erisman et al., 2008; Hu et al., 2014)
  - Associated with acidification and eutrophication of soils and surface waters, which can negatively affect biodiversity (Vitousek et al., 1997; Krupa, 2003; Bobbink et al., 2010)
- Particulate matter, especially that smaller than 2.5 microns ($PM_{2.5}$), poses serious health hazards
  - A major contributor to smog, and affects life expectancy in the United States (Pope et al., 2009) and globally (Giannadaki et al., 2014)
- NH_3 emissions are regulated in some parts of the world (e.g., 1999 Gothenburg Protocol)

NH_3

- Atmospheric NH_3 is rapidly removed by wet and dry deposition as well as by reactions with acids in the atmosphere
  - Thus has a relatively short lifetime ranging from a few hours to a few days (Galloway et al., 2003)
  - NH_3 lifetime may be longer for certain cases, such as biomass burning emissions that inject NH_3 into the free troposphere (Lutsch et al., 2016, 2019)
- Agricultural emissions are major sources of atmospheric NH_3
  - This leads to a peak in spring
- Atmospheric NH_3 abundance is increasing, with trends as high as 12 % annually (Yu et al., 2018)
  - Despite regional emissions regulations, global NH_3 emissions are increasing (Warner et al., 2016; Lachatre et al., 2019)
  - Attributed to increases in agricultural livestock numbers and increased nitrogen fertilizer usage (Warner et al., 2016)

Introduction and Aim

- This study is part of the AmmonAQ project
  - Examining atmospheric NH_3 and how it affects air quality, particularly focusing on $PM_{2.5}$ formation
  - Collaborative project with LATMOS of Paris
  - Uses Toronto and Paris as benchmark cities
    - Recently, Mexico City was also added
- Several studies have looked at utilizing space-bourne measurements of NH_3 in conjunction with ground-based observations (e.g., Dammers et al., 2016)
  - Build on past work, and look at in-situ measurements as well
- Aim of this study is to look for trends in NH_3 over Toronto, and examine how various observations of varying scales compare

Datasets

- Total column data from ground-based Fourier transform infrared (FTIR) Spectroscopy (more on next slide)
  - Total column measurements of numerous gases including NH_3 are made on a regular basis
  - 2002-2018
  - NH_3 along with other urban pollutants
- In-situ measurements of NH_3 (ECCC NAPS) [1]
  - 2014-2017 for downtown Toronto
- IASI satellite NH_3 columns
  - 2008-2018
- Modeled NH_3
  - GEOS-Chem chemical transport model (v11-01)
    - 2 x 2.5 resolution, 2003-2018

[1]http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx

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
  - Part of NDACC (Network for the Detection of Atmospheric Composition Change)
    - International network of observing stations
  - The FTIR spectrometer is coupled to an active solar tracker with housing
  - Operation is semi-automated
  - Can be remotely accessed/operated

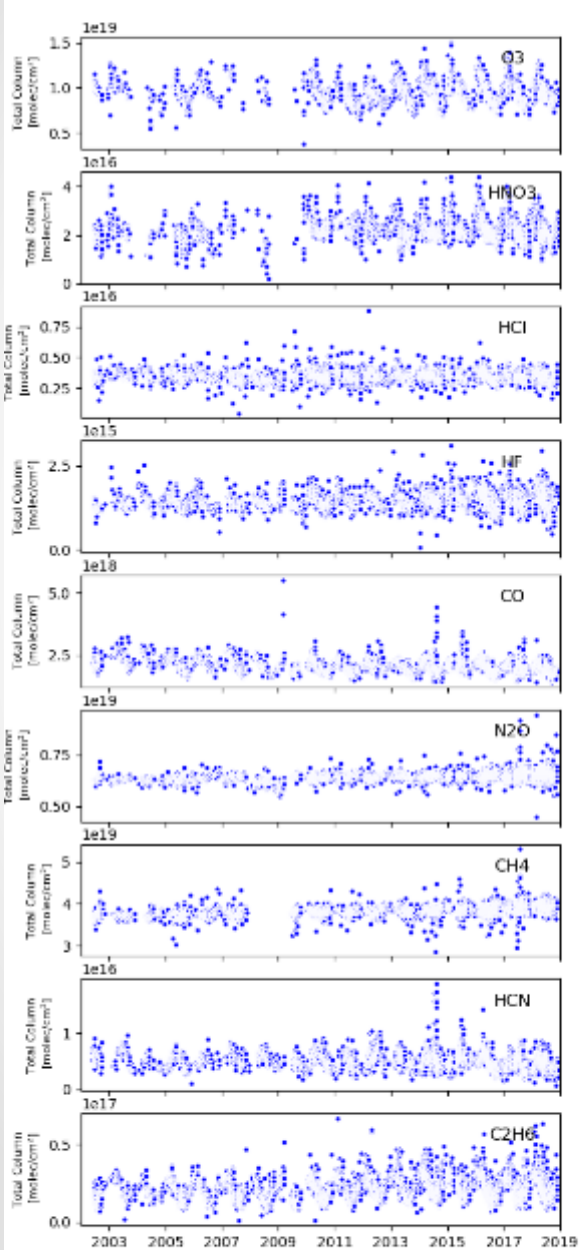
Methods

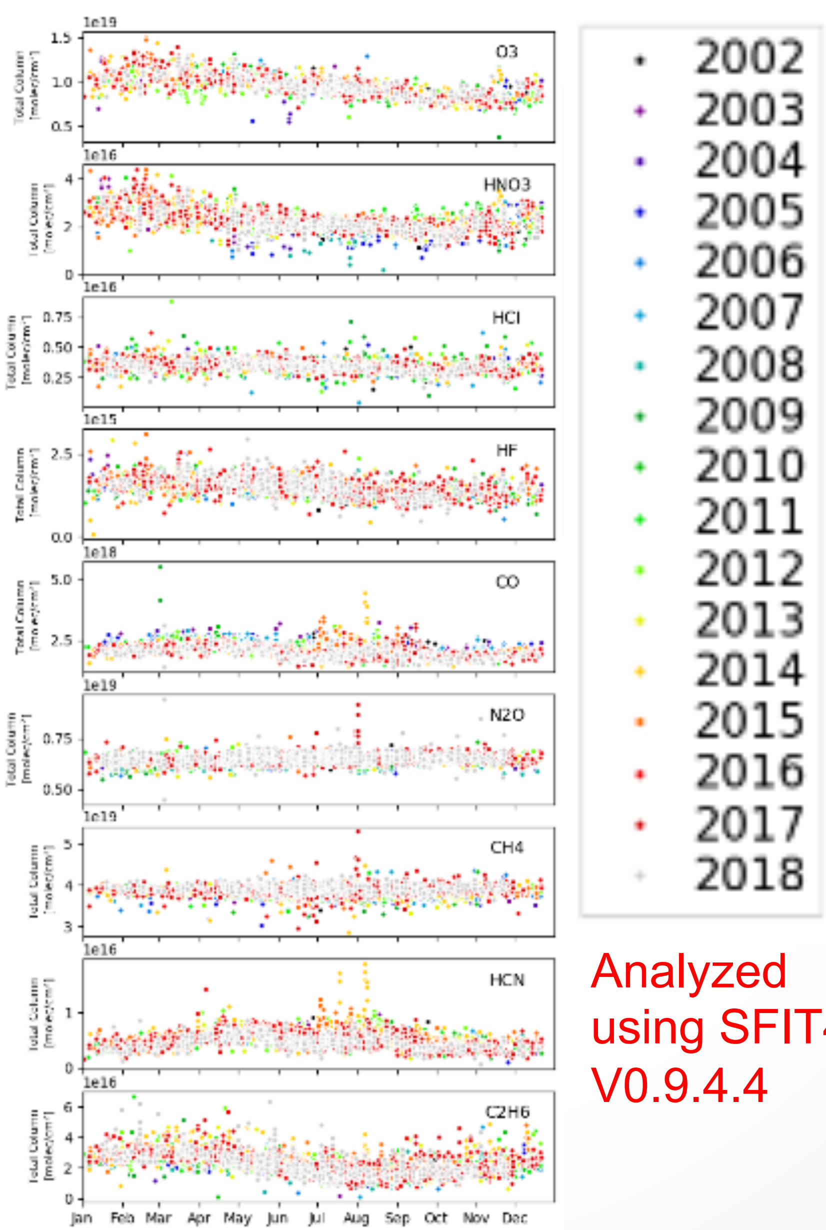
- Trends was examined by fitting a trended Fourier series of order 3
  - Error analysis using Bootstrap resampling (Gardiner et al., 2008) and Weatherhead method (Weatherhead et al., 1998), NH_3 along with other urban pollutants
  - The fit was used to identify enhanced outliers as well (Zellweger et al., 2009)
- Surface and column (NAPS vs. TAO) comparison was done by utilizing standardized columns (following Viatte et al., 2019):

$$X^{i}_{\text{standardized}} = \frac{X_i - \mu_X}{\sigma_X}$$

  - i.e. each observation is centered around 0 and normalized by the standard deviation of the dataset
- IASI and TAO columns were compared by various coincidence criteria, ranging from
  - 25 km to 100 km spatial criteria and 20 minutes to 90 minutes temporal criteria
- GEOS-Chem data were compared against both TAO data (point measurement) and IASI, for assessing model performance on various scales

TAO FTIR Time Series: 2002-2018





Total columns for IRWG standard gases

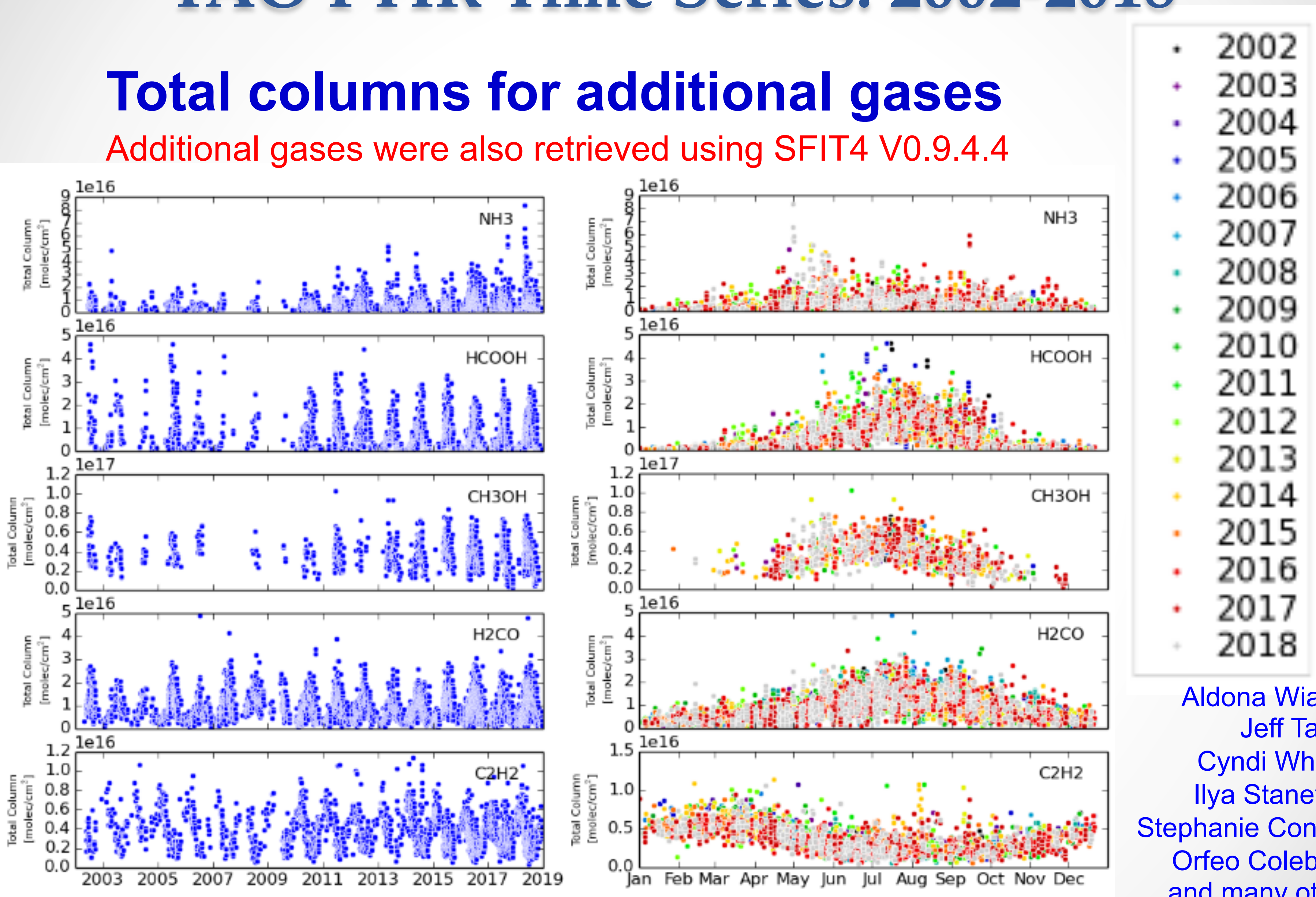
Analyzed using SFIT4 V0.9.4.4

Aldona Wiacek,
Jeff Taylor,
Cyndi Whaley,
Ilya Stanevich,
Stephanie Conway,
Orfeo Colebatch
and many others
Plot: Shoma Yamanouchi

TAO FTIR Time Series: 2002-2018

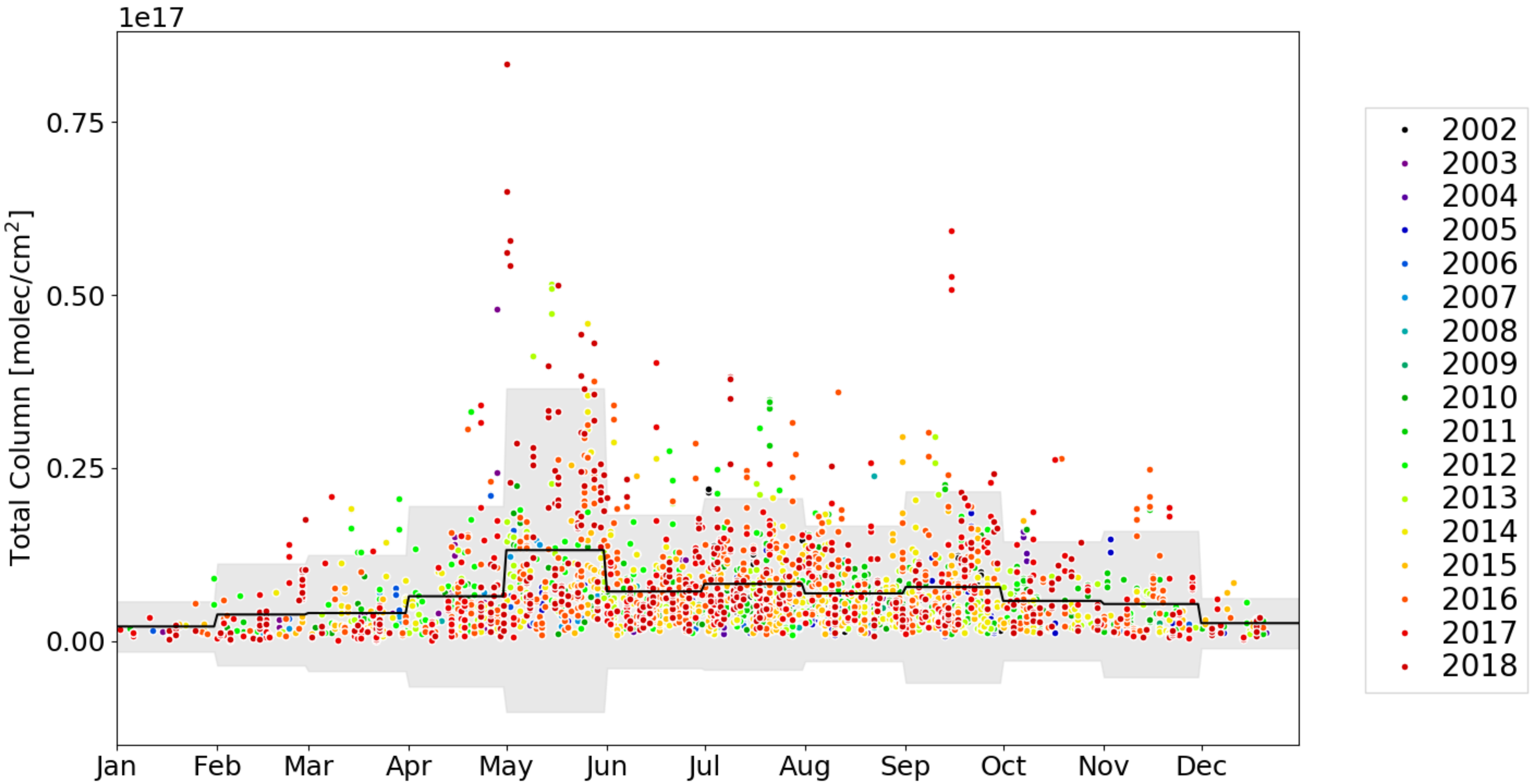
Total columns for additional gases

Additional gases were also retrieved using SFIT4 V0.9.4.4



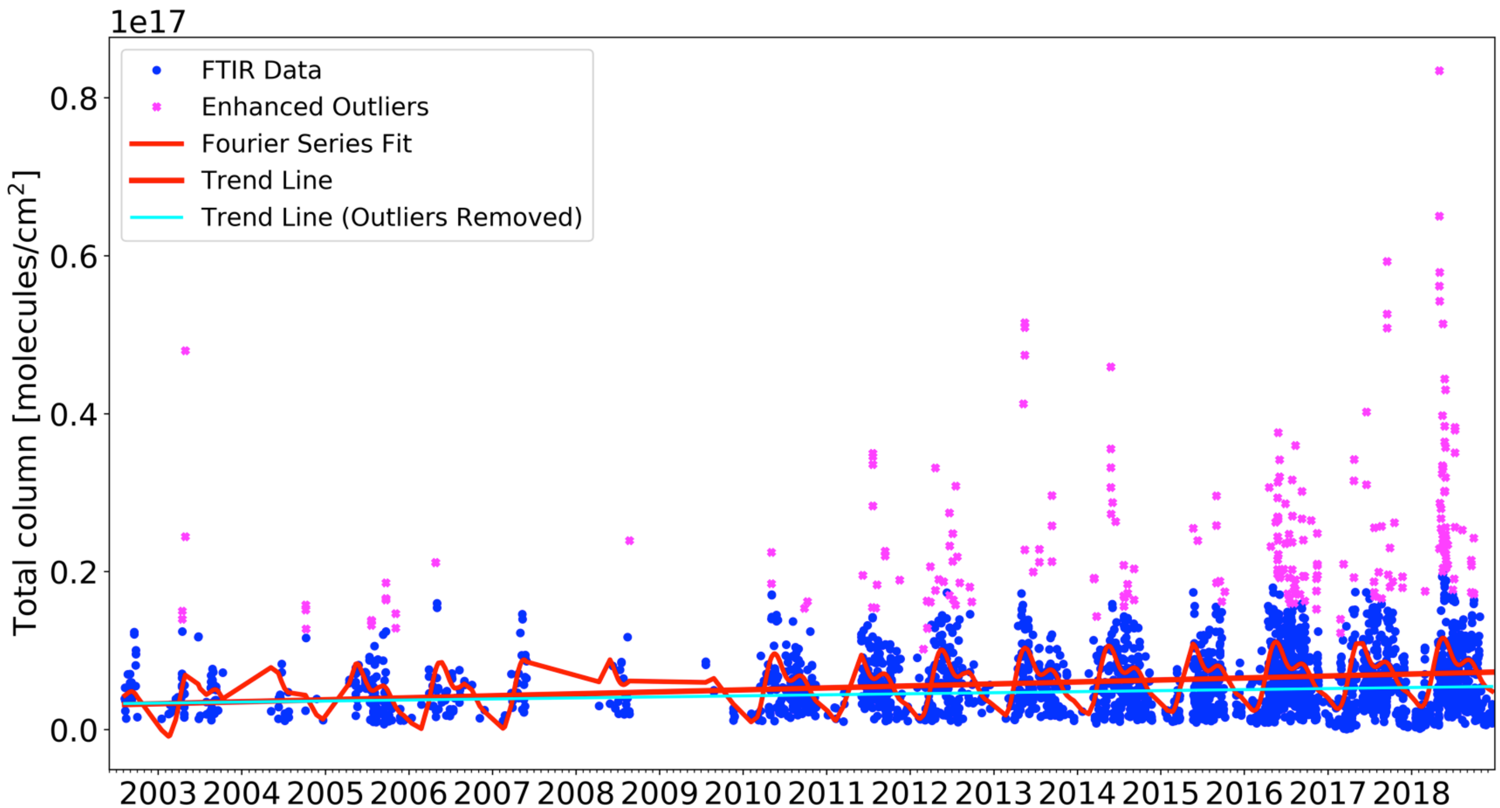
Aldona Wiacek,
Jeff Taylor,
Cyndi Whaley,
Ilya Stanevich,
Stephanie Conway,
Orfeo Colebatch
and many others
Plot: Shoma Yamanouchi

TAO NH_3



TAO total columns of NH_3 from 2002 to 2018 plotted from January to December. Monthly averages and ± 2σ are indicated by the black line and shading, respectively.

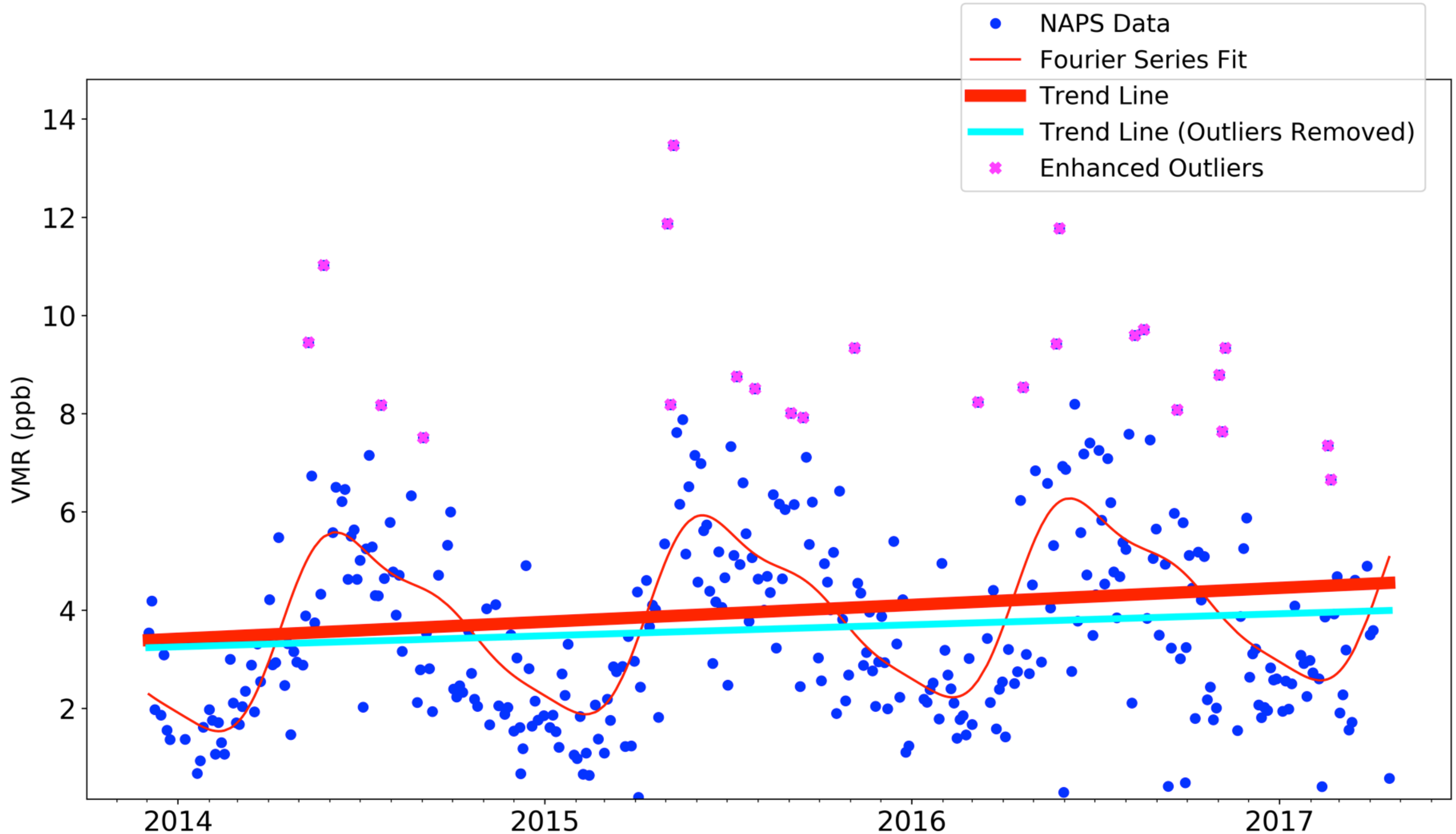
TAO NH_3



TAO time series of NH_3 total columns (molecules/cm^2) from 2002 to 2018 with trends and fit. Trend of 3.34 ± 0.46 %/year and 2.23 ± 0.79 %/year (2σ confidence interval from bootstrap resampling), with and without outliers, were observed.

2σ significance with 33.8 years and 29.3 years of measurements, with and without outliers.

NAPS NH_3

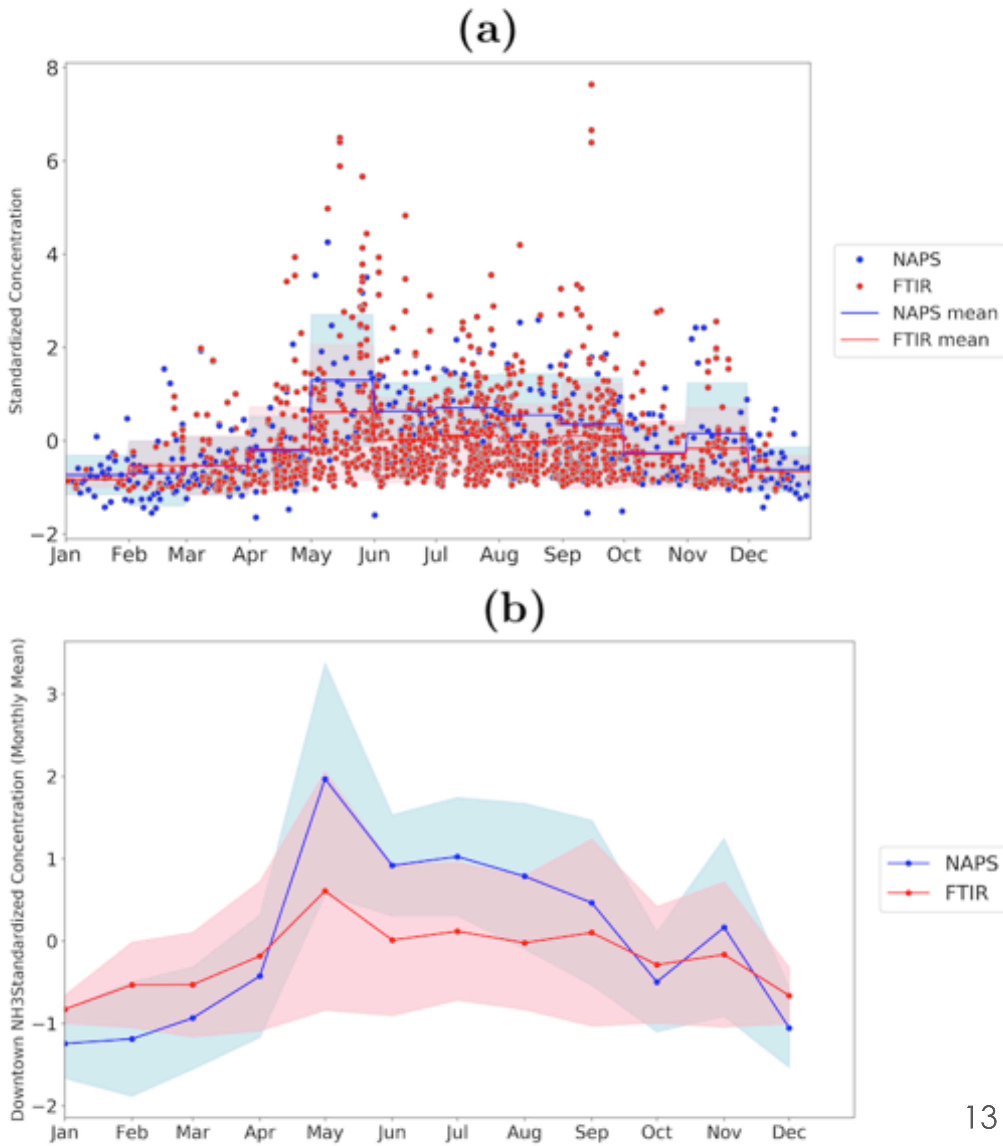


NAPS time series of NH_3 surface VMR from 2013 to 2017 with trends and fit.
Trends of 8.88 ± 2.83 %/year and 6.40 ± 0.18 %/year (2σ confidence interval from bootstrap resampling), with and without outliers, were observed.
2σ significance with 8.4 years of measurements.

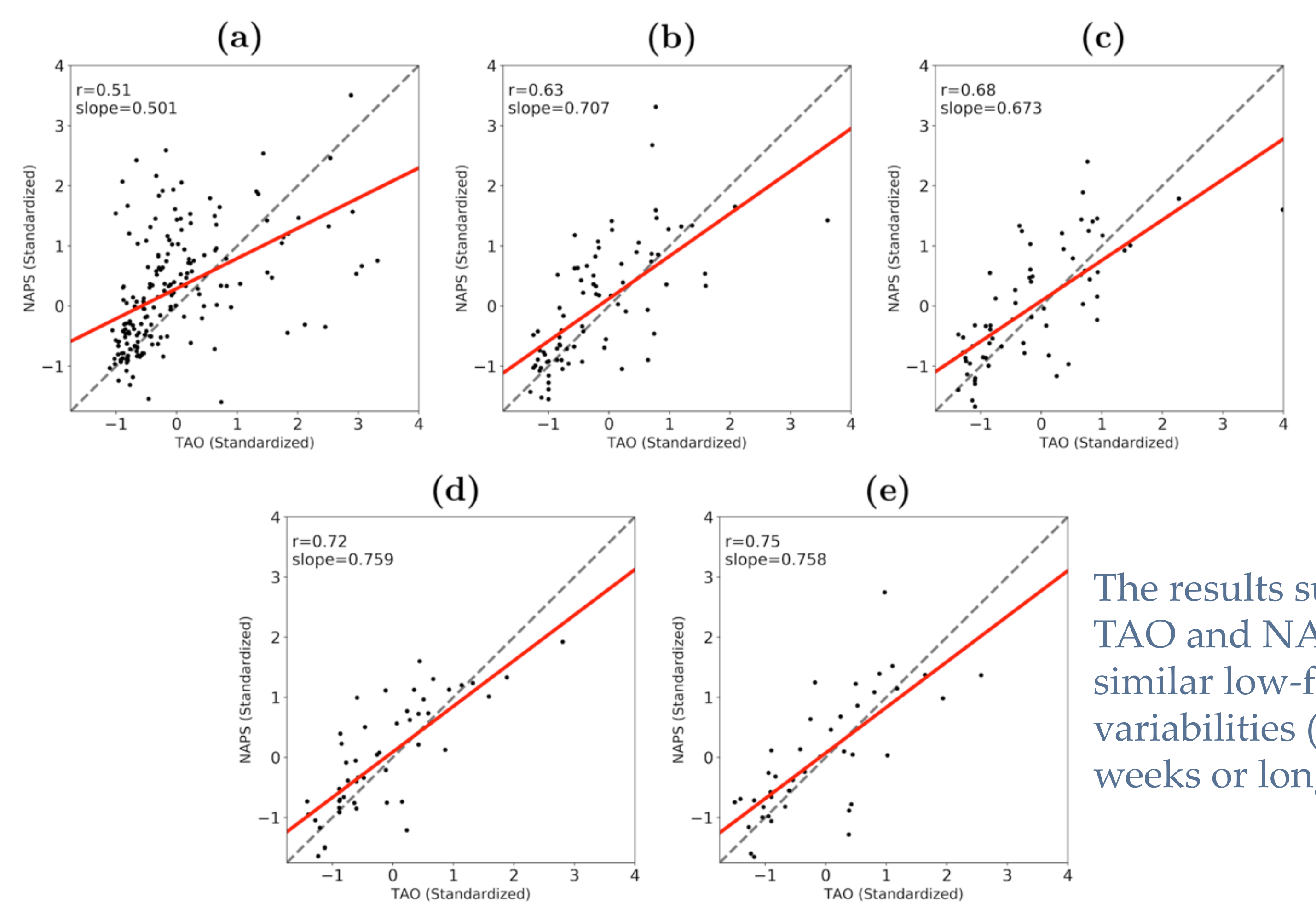
NAPS TAO Correlation

(a) The standardized TAO total column and NAPS surface VMR of NH_3 plotted from January to December. Monthly averages and ± 1σ are indicated by the red and blue lines and shading for TAO and NAPS, respectively.

(b) The standardized TAO NH_3 total column (red) and NAPS surface NH_3 VMR (blue) monthly averages lines with their respective ± 1σ (shading).



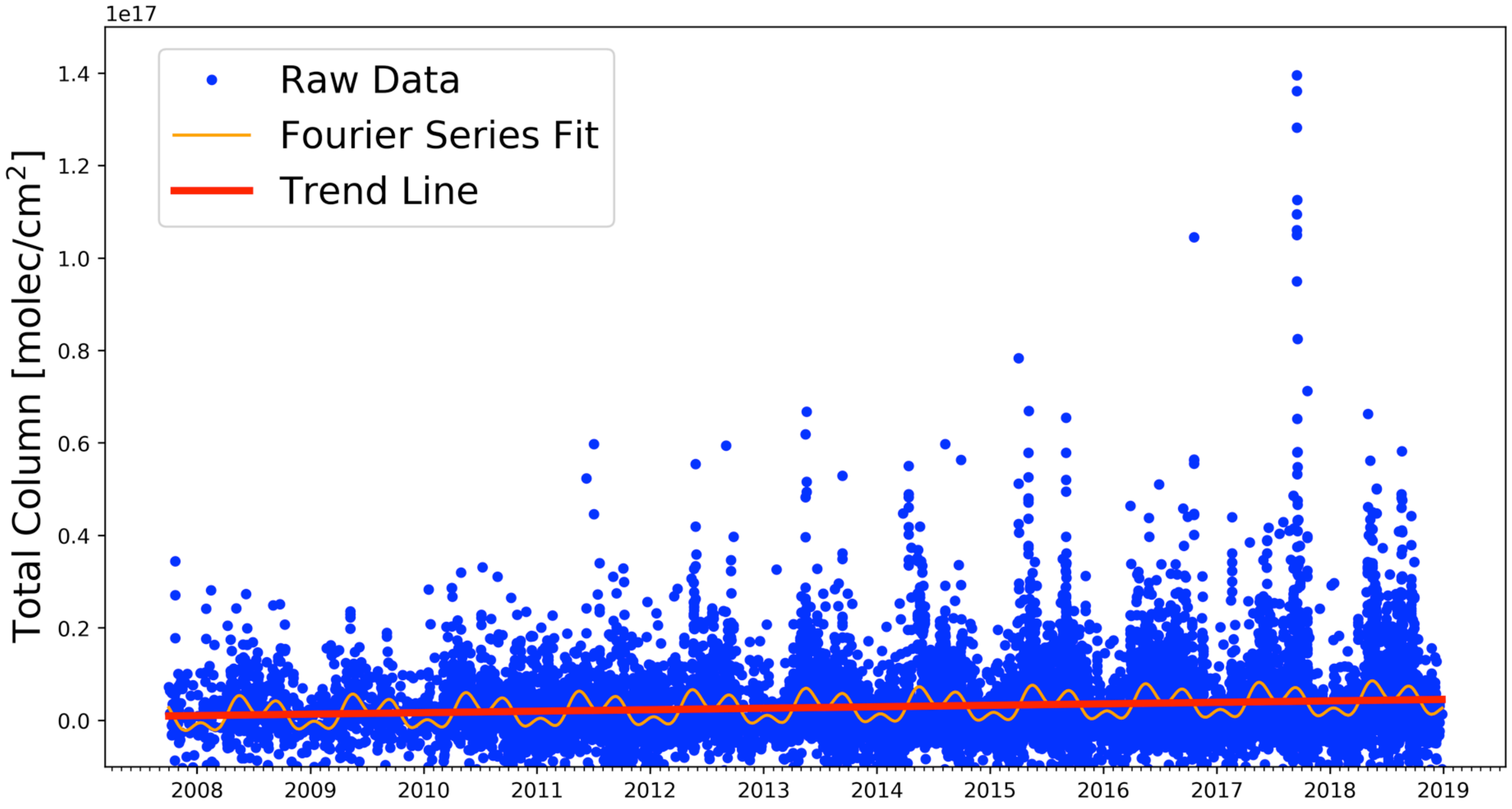
NAPS TAO Correlation



The results suggests that TAO and NAPS see similar low-frequency variabilities (period of 2 weeks or longer) in NH_3.

Standardized TAO NH_3 total column plotted against standardized NAPS NH_3 surface VMR. (a) shows the raw comparison, where for each NAPS observation, the closest daily average TAO measurement, if there are any within 72 hours, is plotted. (b), (c), (d) and (e) show standardized TAO NH_3 total column plotted against standardized NAPS NH_3 surface VMR, resampled to 15-day, 18-day, 24-day and monthly averages, respectively.

IASI NH_3



Time series of IASI NH_3 total column observations made within 50 km of TAO. The fit and the trend line are shown in orange and red, respectively. Observed trend was 8.38 ± 0.77 %/year

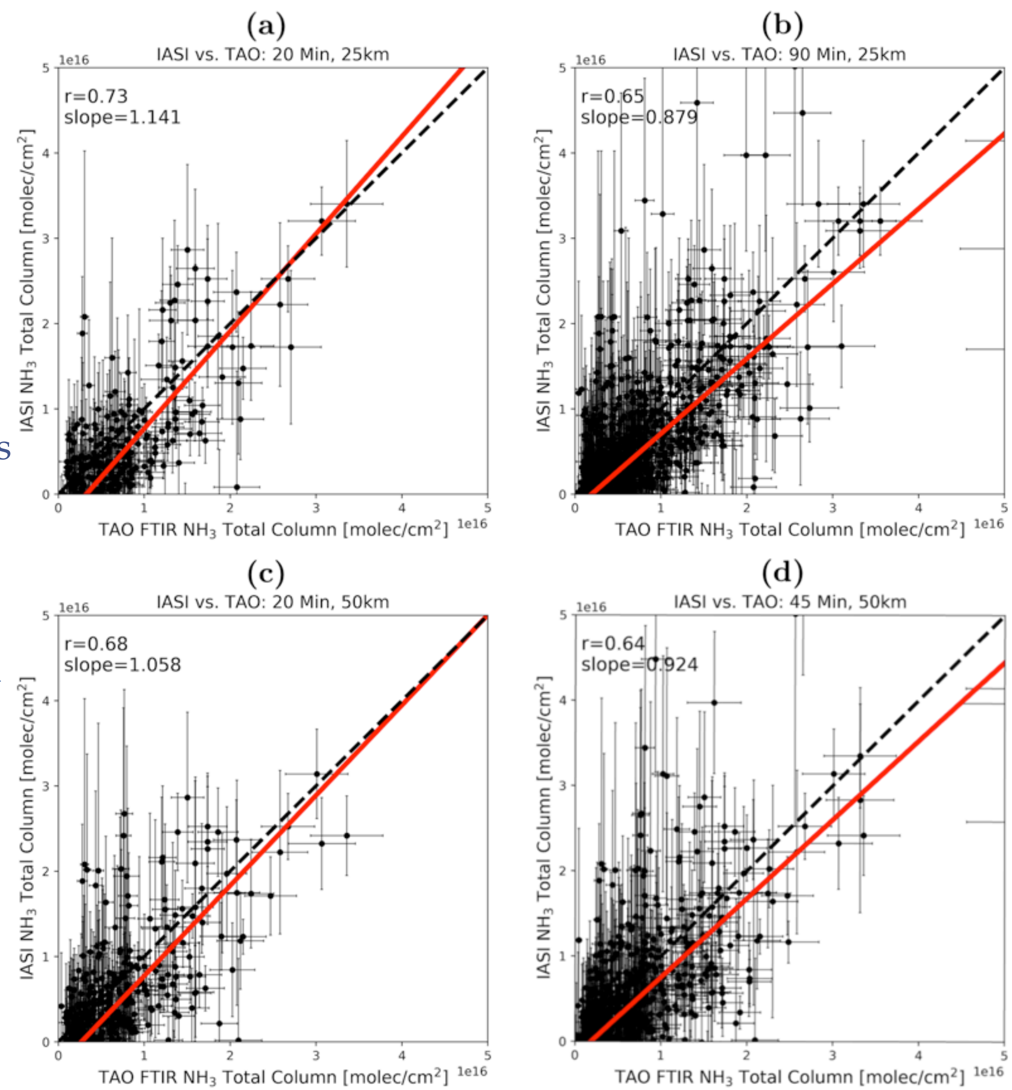
IASI TAO Correlation

TAO FTIR NH_3 total column and IASI NH_3 total column correlation plot, with the coincidence criteria of:

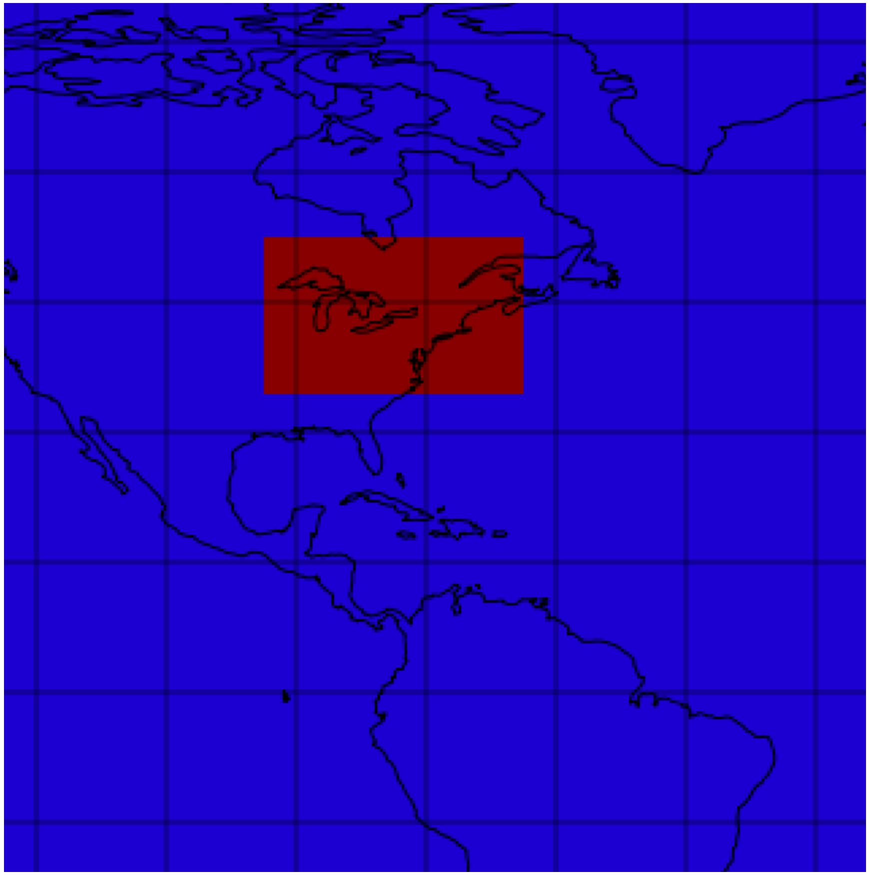
(a) 20 minutes and 25 km,
(b) 90 minutes and 25 km,
(c) 20 minutes and 50 km, and
(d) 45 minutes and 50 km.

Data from 2007 to 2018 are plotted. Dashed lines indicate slope = 1, while the red lines are the lines of best fit. Error bars are from reported observational uncertainties.

The best correlation was achieved when using measurements made within 20 minutes and within 25 km of each other, which resulted in r = 0.73 and slope of 1.141. Coincidence criteria of 20 minutes and 50 km gave r = 0.68 and slope = 1.058. Criteria of 45 minutes and 50 km also shows a correlation comparable to the 90 minutes, 25 km criteria (used by Dammers et al. (2016)), with r = 0.64 and slope = 0.924. This suggests that TAO FTIR is a good indicator of NH_3 concentrations on a city-wide scale (~50 km).

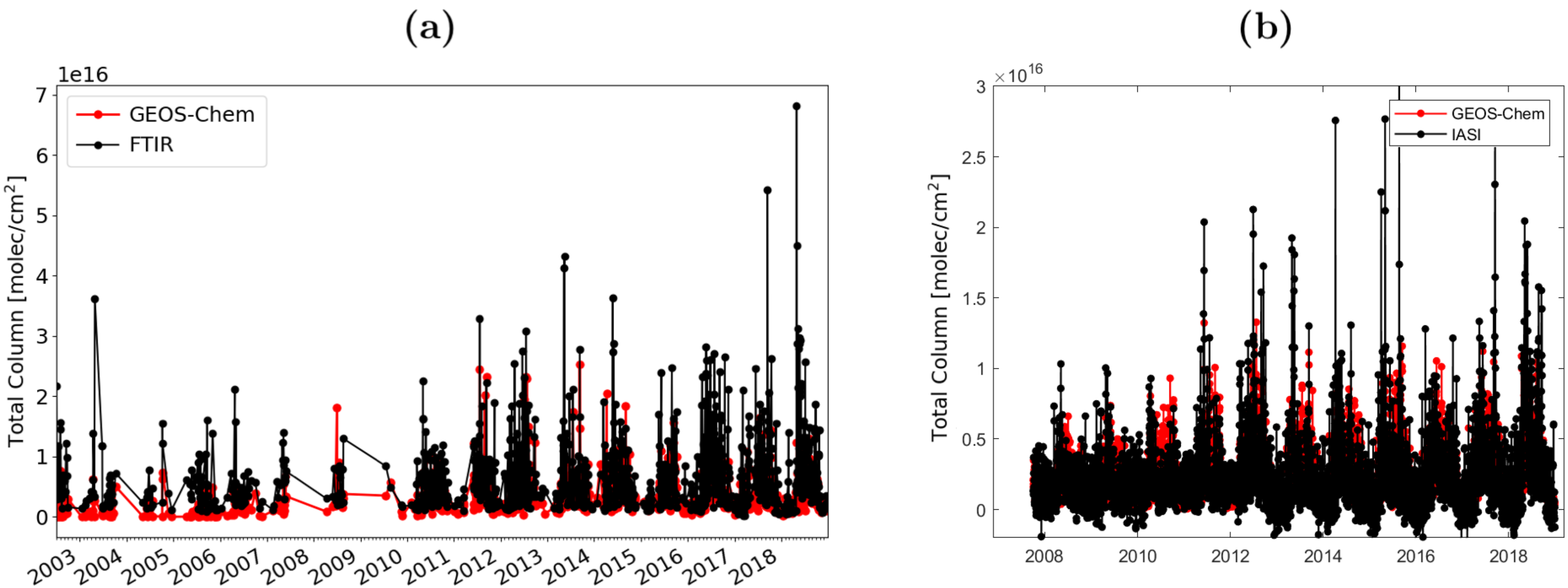


GEOS-Chem Grids



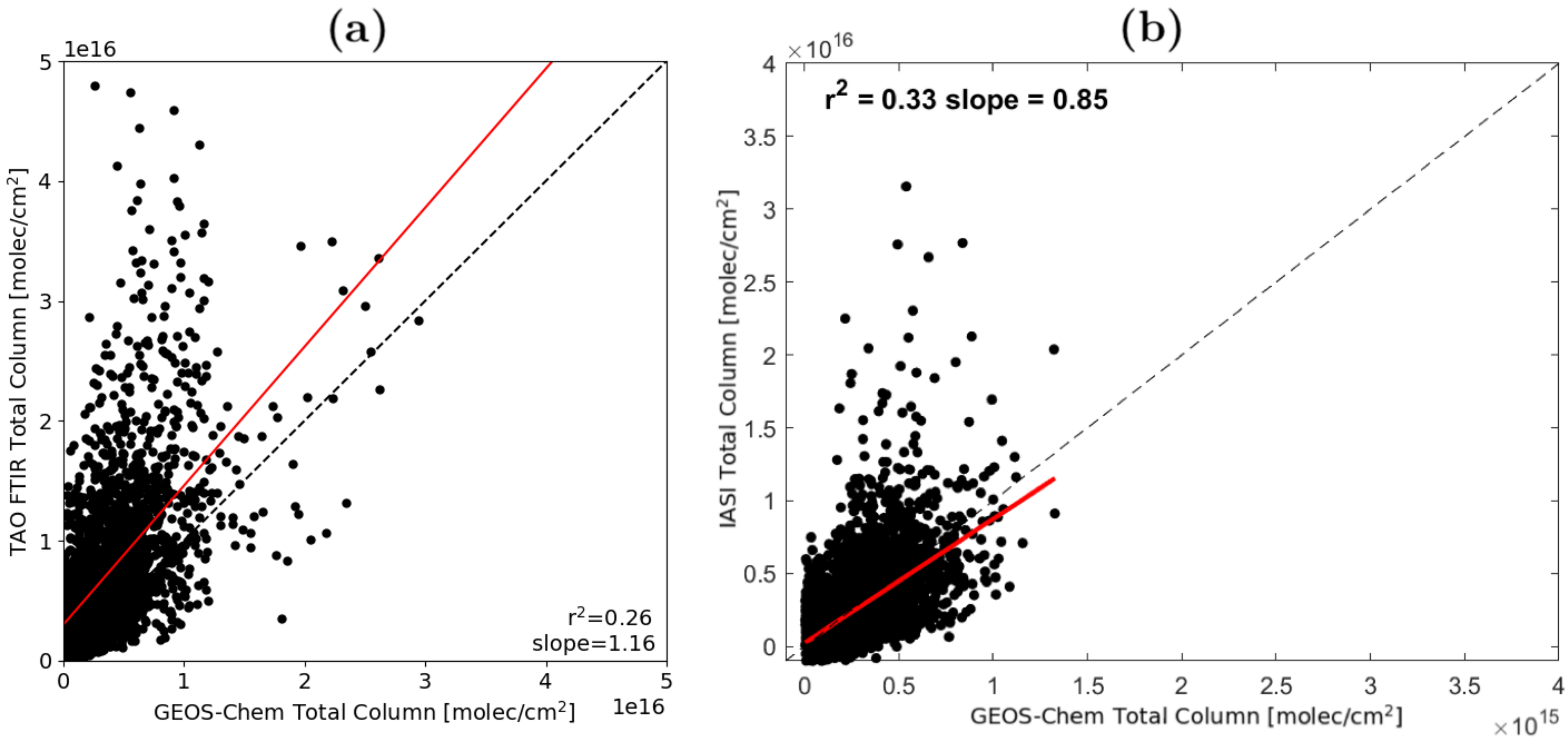
- GEOS-Chem (2°x2.5°)
- Single cell over Toronto, as well as a larger regional domain (spanning from 35°N to 53°N, and 93.75°W to 63.75°W) was used in this study to assess model performance
  - Regional domain used for this project is shown here

GEOS-Chem Comparison



(a) GEOS-Chem and TAO FTIR NH_3 total columns from 2002 to 2018. (b) GEOS-Chem and IASI NH_3 total columns (averaged over domain spanning from 35°N to 53°N, and 93.75°W to 63.75°W) from 2008 to 2018.

GEOS-Chem Comparison



Correlation plots of (a) TAO vs. GEOS-Chem NH_3 total columns, and (b) IASI vs. GEOS-Chem NH_3 total columns (large domain). Data from 2002 to 2018 are plotted for TAO and data from 2008 to 2018 are plotted for IASI.

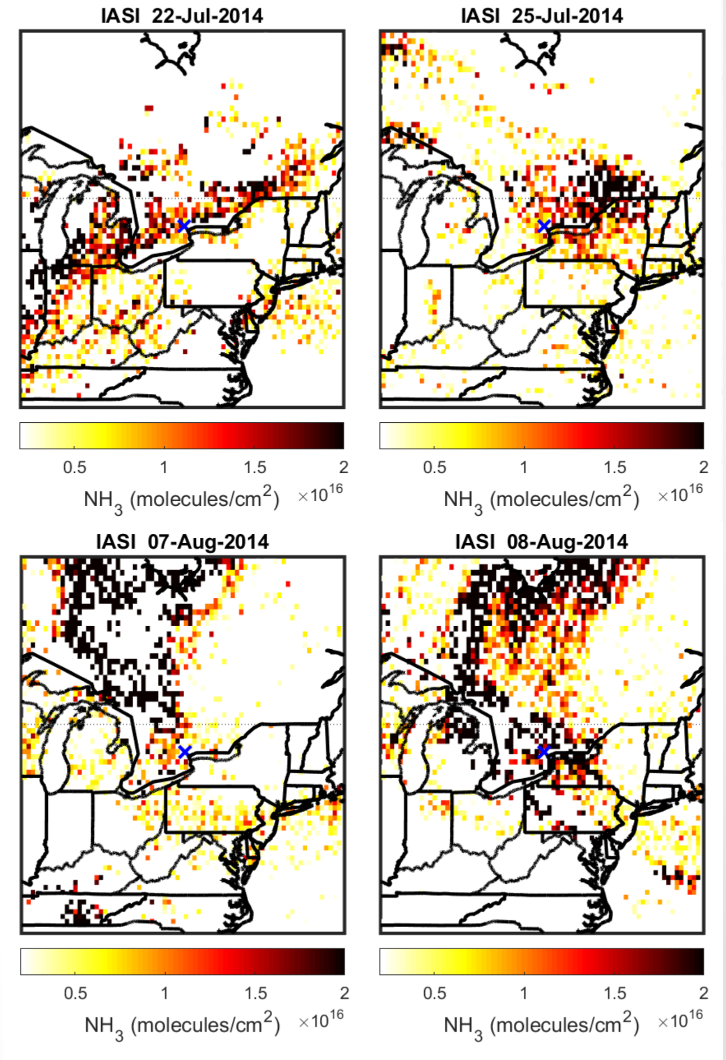
GEOS-Chem Comparison

- The spatial coincidence was calculated by binning the IASI data into the grids of GEOS-Chem
- Temporal coincidence was done by calculating the mean overpass time in the domain and averaging the model data between one hour before and one hour after the mean overpass time
- Comparison with IASI in the larger domain showed better correlation than GEOS-Chem against TAO FTIR, with $r^2 = 0.33$ (TAO was 0.26)
  - Slope was 0.85, meaning NH_3 is overestimated in GEOS-Chem when compared to IASI at this scale
- Correlation using one grid cell over Toronto resulted in no correlation, at $r^2 = 0.13$
- Results indicate GEOS-Chem is able to model NH_3 are larger regional scales, but a finer resolution is needed for better comparison with smaller regions

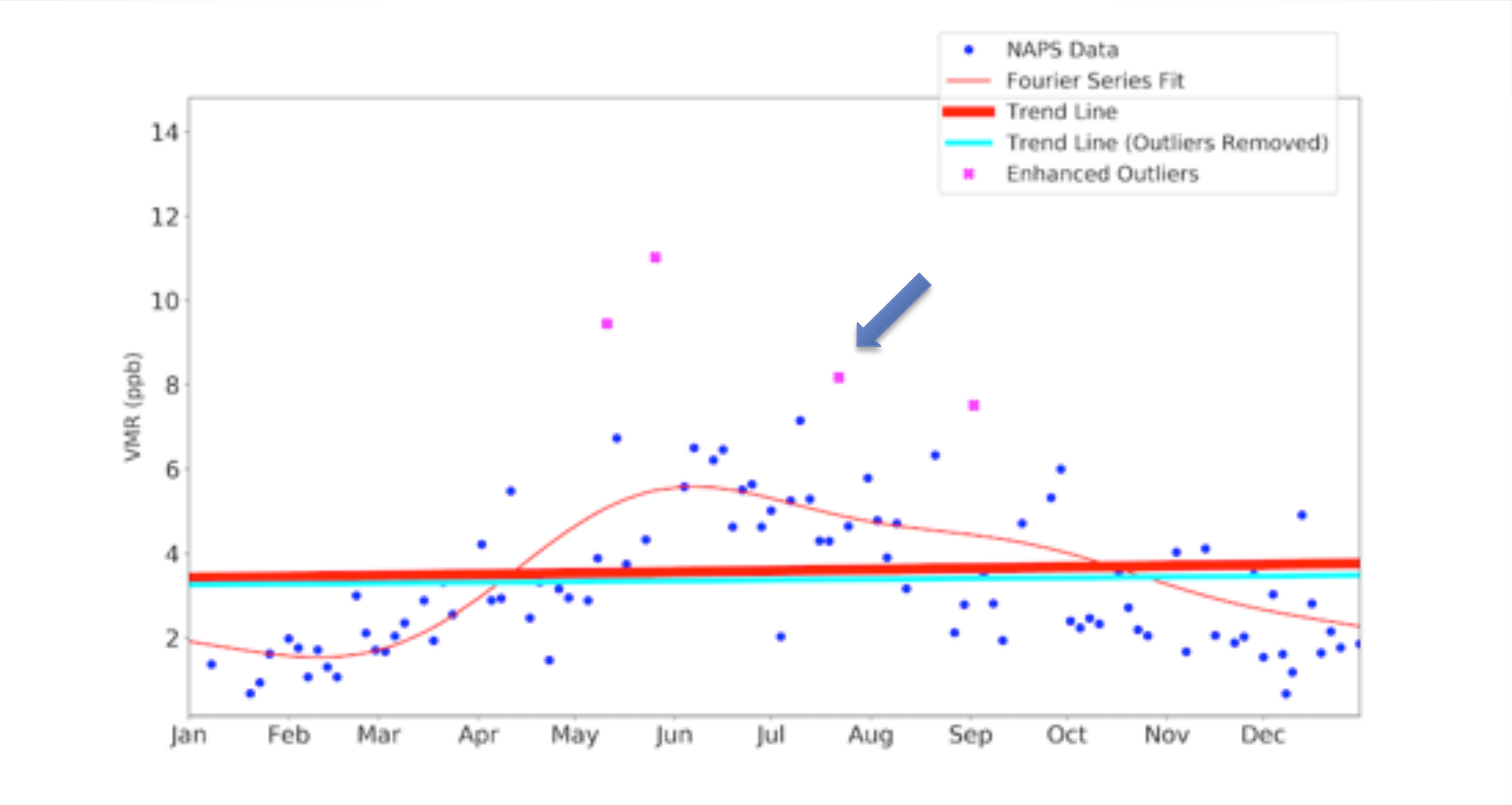
Case Study

2014 fire events enhancing surface NH_3

- Large fires in August, 2014 led to enhanced CO, HCN, C_2H_6 and NH_3 over Toronto (Lutsch et al., 2016)
- The Zellweger et al. (2009) enhancement analysis showed enhancements in not only TAO NH_3 but also surface NH_3 as well
- Right plot shows IASI also detecting NH_3 plumes traveling over Toronto



2014 Fire event continued

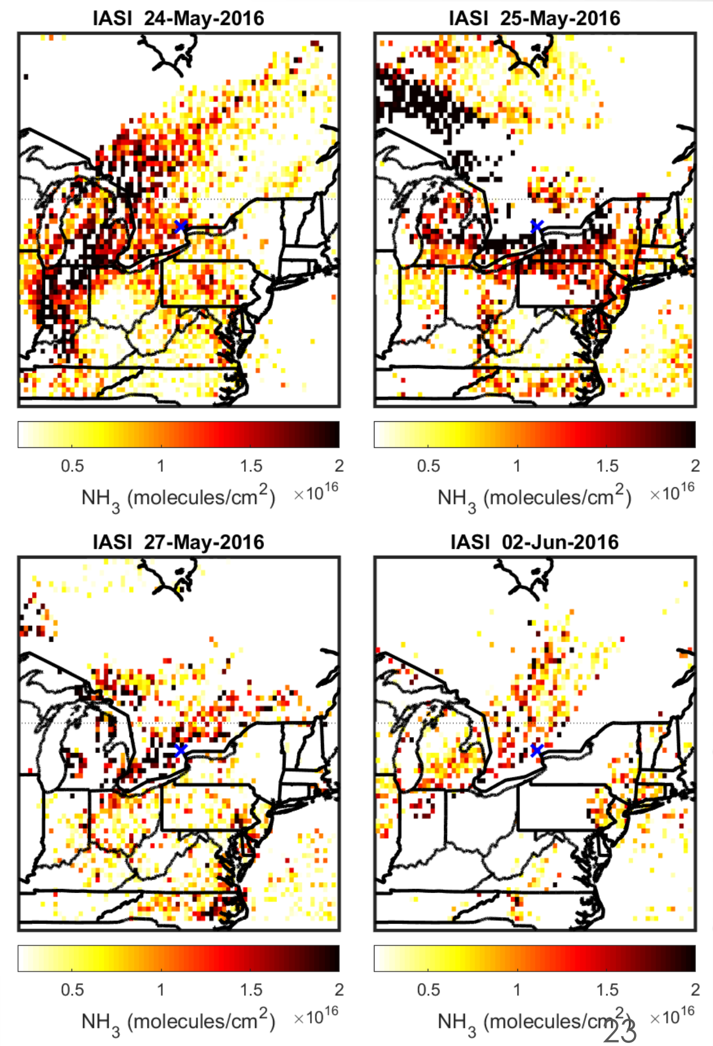


- TAO NH_3 was enhanced on 22 July, 25 July, 7 and 8 August, with a maxima on 22 July.
- NAPS surface NH_3 in 2014 is shown above. Enhancement event was found on 22 July.

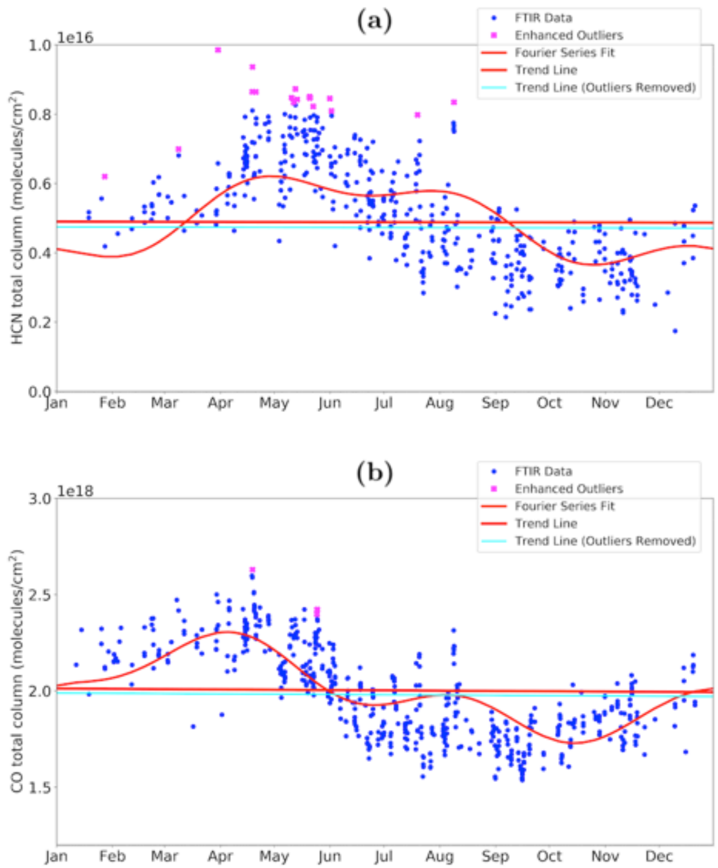
Case Study

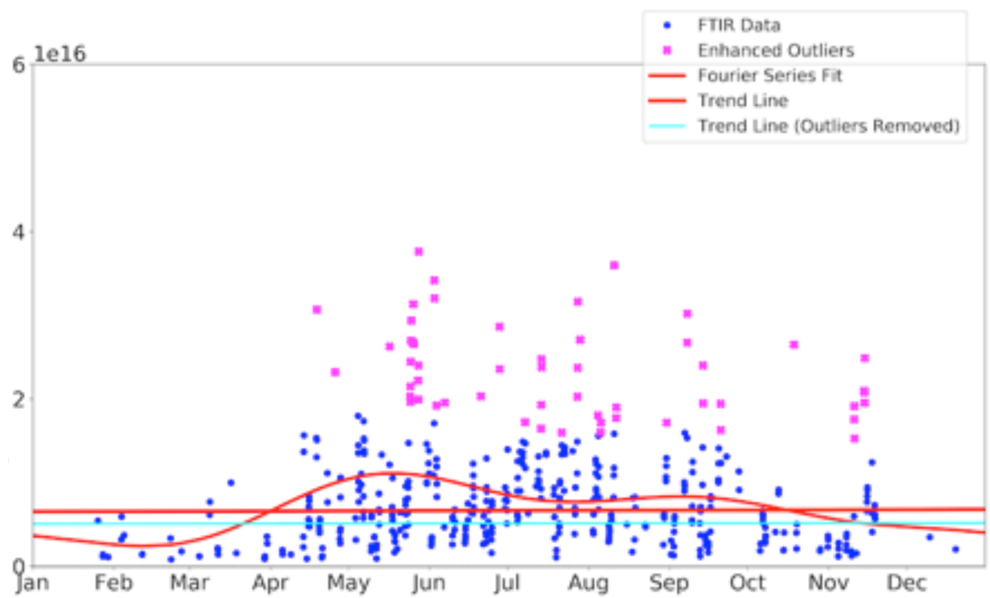
2016 fire events enhancing surface NH_3

- Large fires in May, 2016 in Fort McMurray, Alberta
- Affected air quality (surface ozone) as far as Connecticut (Connecticut Department of Energy and Environmental Protection, 2017)
- TAO columns as well as surface NH_3 wereenhanced
- Right plot shows IASI detecting NH_3 plumes traveling over Toronto



2016 Fire event continued

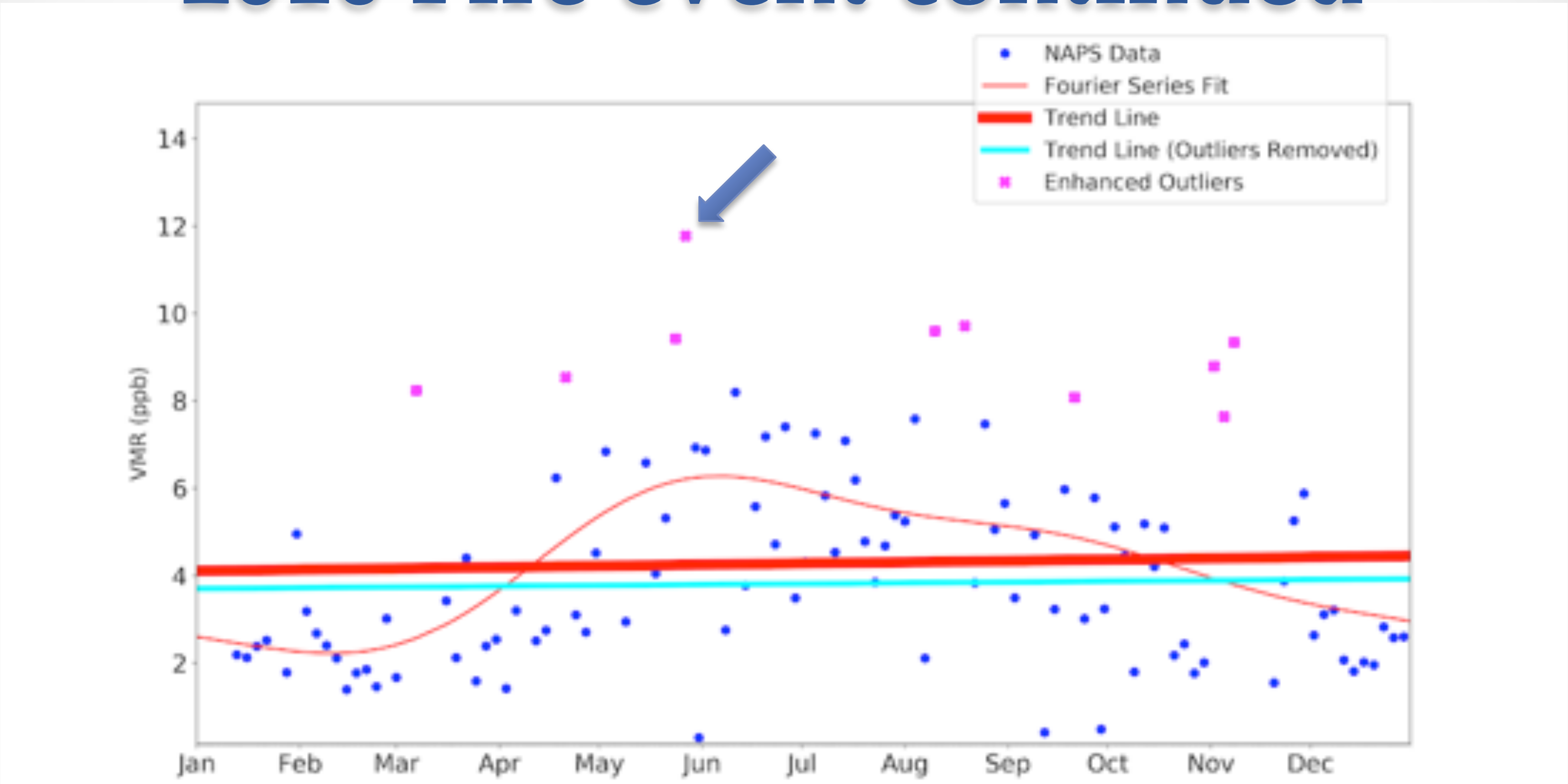




- (a) TAO HCN were enhanced on 20 May, 22 May, 31 May, and on 1 June.
- (b) TAO CO was enhanced on 24 May.

- Above shows TAO NH_3 for 2016.
- Enhanced outliers seen on 24, 25, 27 May and 2, June.
- Maxima occurred on 27 May.

2016 Fire event continued



- Above shows NAPS surface NH_3 in 2016. Enhancement event was found on 24 and 27 May.
- Maxima (shown in plot) occurred on 27 May, same as TAO
- It should be noted that, since NH_3 levels peak in May, identifying pollution events around this timeframe is difficult.
    - However, the existence of pollution events obtained from analyzing the residuals of the Fourier series fit, which accounts for the seasonal cycle contribution to the higher NH_3 (Zellweger et al., 2009), gives credence to these outliers being due to the wildfire plume (or at the very least, due to some outside factor).

Summary

- TAO, IASI, NAPS and GEOS-Chem were used to examine NH_3 variability over Toronto on multiple scales

- Trends in NH_3 over Toronto were observed:
  - All datasets show increasing trends

- TAO NH_3 columns is able to capture seasonality of surface measurements, and comparison with IASI indicates TAO has a city-wide-scale observational footprint

- GEOS-Chem model comparisons with TAO and IASI indicate that higher resolution runs of the model are needed to capture NH_3 variability

- Simultaneous enhancements in TAO (columns) and NAPS (surface) NH_3 were detected during wildfire events