The question of the methane increase through the retrieval of its isotopologues from FTIR ground-based observations

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Background information - Atmospheric methane

- 2nd most important anthropogenic greenhouse gas
- 1/5 of anthropogenic radiative forcing since 1750 is due to methane
- 3 types of emission processes (Kirschke et al., 2013):
    - Biogenic (wetlands, livestock, waste, rice cultivation, termites, ocean and hydrates)
    - Thermogenic (Biomass burning)
    - Pyrogenic (coal mining and gas and oil transport and exploitation)
- New high of 1845 ± 2 ppb (WMO, 2016)
- + 260% increase since 1750 (WMO, 2016)
- + ~0.3 %/year since mid-2000s (Bader et al., 2017)
- Changes remain unexplained

First development and optimization of the retrieval strategy for CH_3D from FTIR (Fourier Transform Infrared) ground-based solar observations

A priori CH_3D vertical mixing ratio profiles from Whole Atmosphere Community Climate Model (WACCM v.4, Marsh et al., 2013) simulation run over 3 years (Buzan et al., 2016); water vapor mixing ratio profiles from daily averages NCEP reanalysis, ozone monthly averaged profiles (1980-2020) from a WACCM simulation (v6) have been used as a priori.

In order to minimize residuals, the best combination of available spectroscopic linelists has been determined :

CH_4 and isotopologues

Spectroscopic linelist for GGG2014, TCCON data archive developed by Toon et al. (2014)

Water vapour

Experimental linelist of water vapor line parameters developed by Loos et al. (2017a and 2017b)

Interfering species

The HITRAN 2008 compilation (Rothman et al., 2009), for other interfering species, including O_3.

How can isotopologues help ?

Heavier molecules of methane, isotopologues, are emitted and depleted with different **isotopic ratios** depending on the emission sources or removal pathway (**see Figure 1**) and show specific delta values.
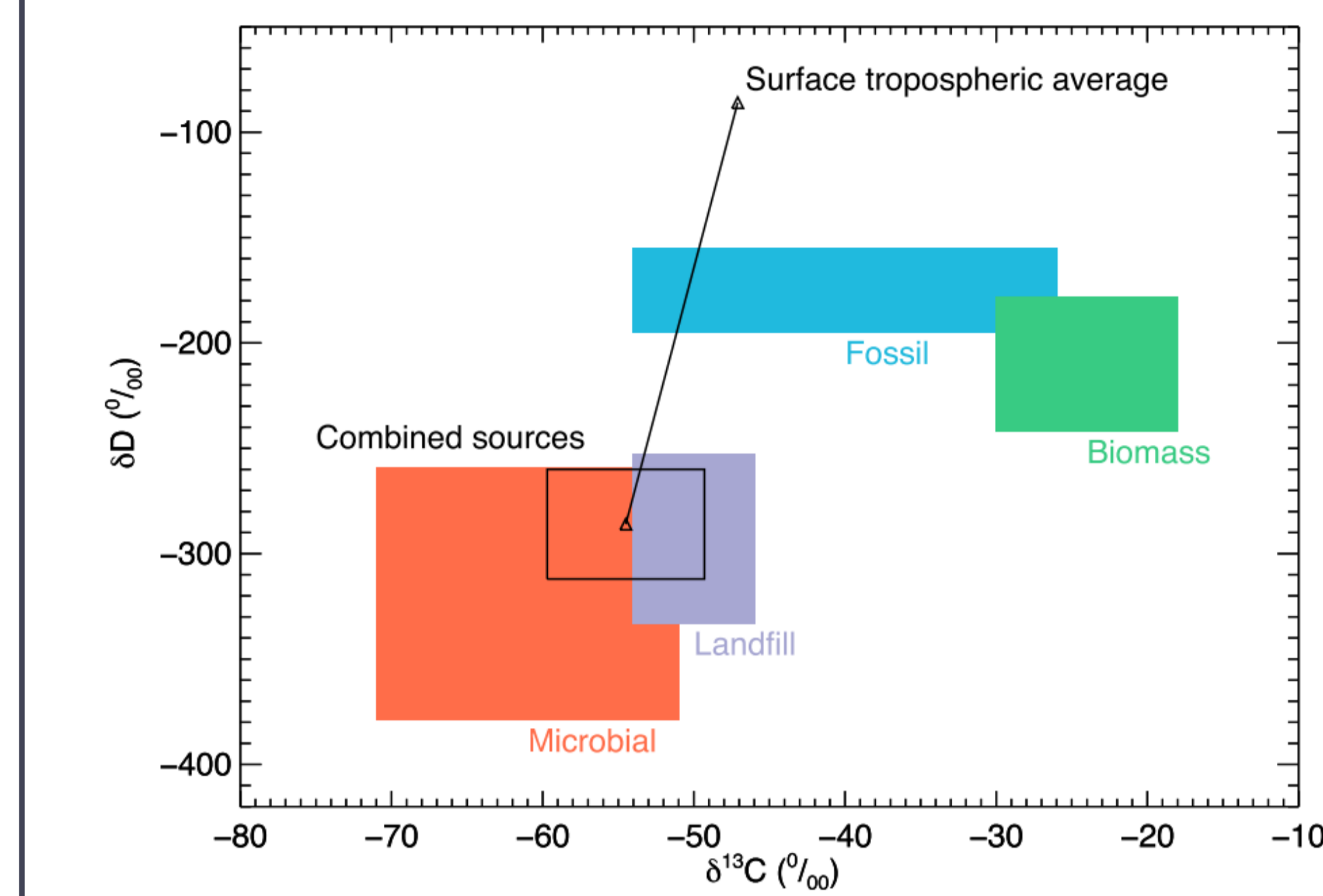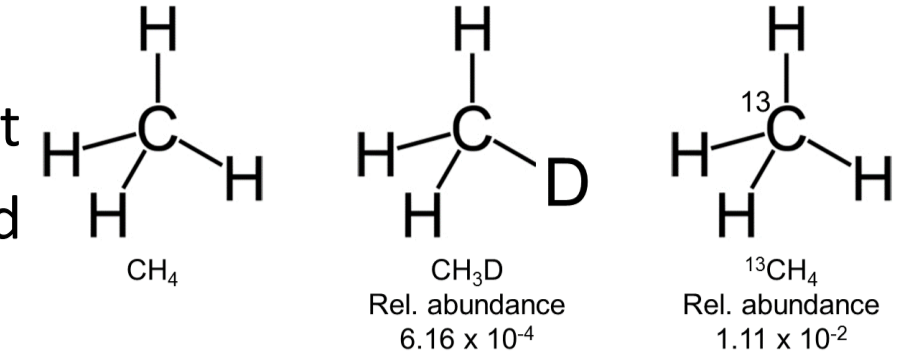
Determining the $^{13}C/^{12}C$ and D/H content of atmospheric methane is therefore a unique tracer of its budget and can provide additional constraints on the regional, hemispheric and global budgets (Snover and Quay, 2000).

Figure 1 - The $\delta^{13}C$ and δD for the four major sources whose emissions were estimated in Rigby et al. (2012). (Figure 2 from Rigby et al., 2012).

Spectral windows

4 spectral windows containing CH_3D absorption lines have been carefully identified in order to minimize interefences.

Figure 2 - Averaged observed (in dark green) and calculated (in red "x") spectra (lower frame) as well as residuals in % (grey line in upper frame) derived from a representative set of observations (222 spectra) collected at Toronto during 2005. The individual contributions of each interfering gas have been vertically displaced for clarity.

Window limits are (A) 2950.7 - 2951, (B) 3070.71 - 3073.15, (C) 3072.7 - 3073.15, (D) 2089.15 - 2089.7 cm^{-1}.
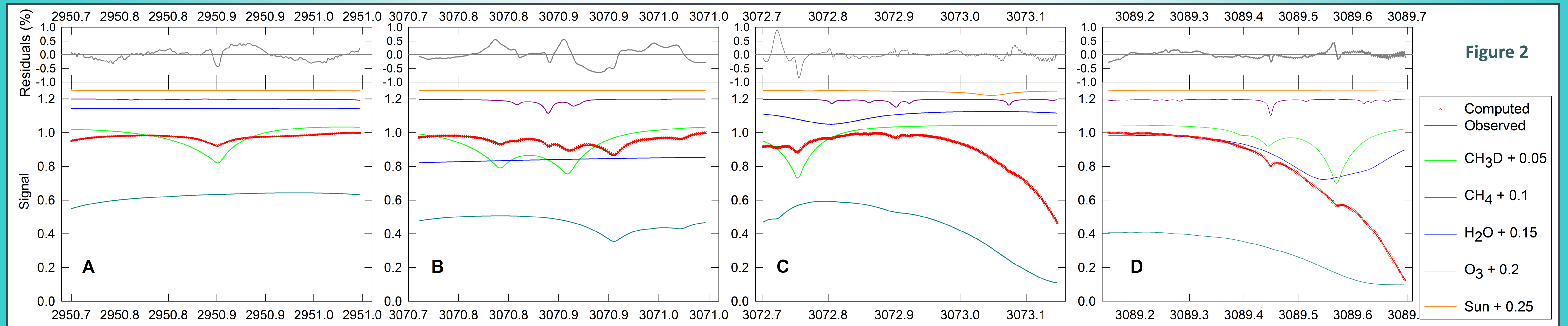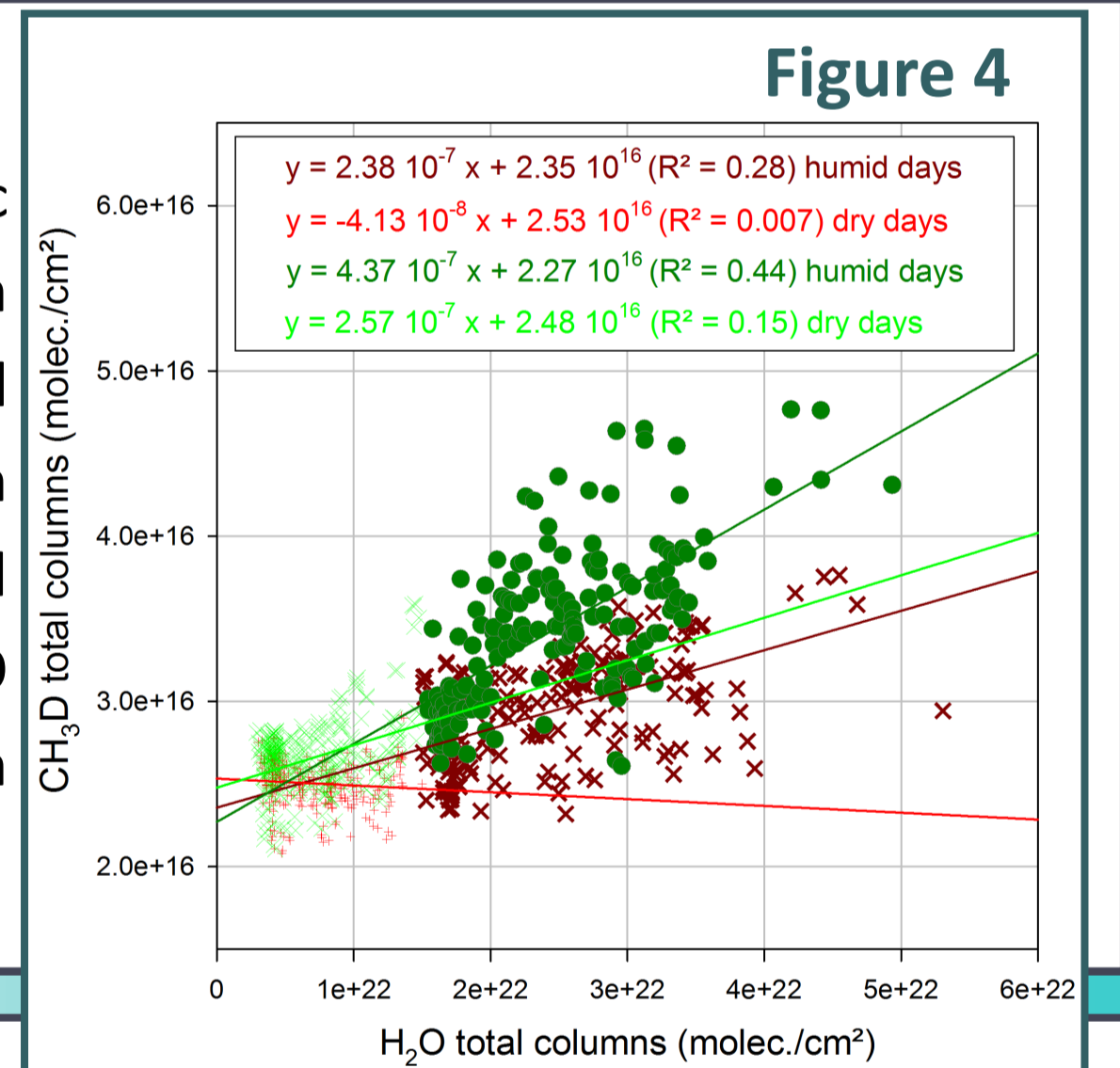

Figure 2

The benefit of 4 windows

Figure 3 illustrates the error budget (Rodgers, 1990) depending on the use of 4 windows for both Toronto and Eureka measurements. Using 4 windows (A+B+C+D, in pink) allows us to simultaneously decrease measurement and smoothing errors while improving the Degrees of Freedom for Signal (DOFS). These can reach values as high as 1.43 (Toronto) and 3.95 (Eureka), see Fig. 6.
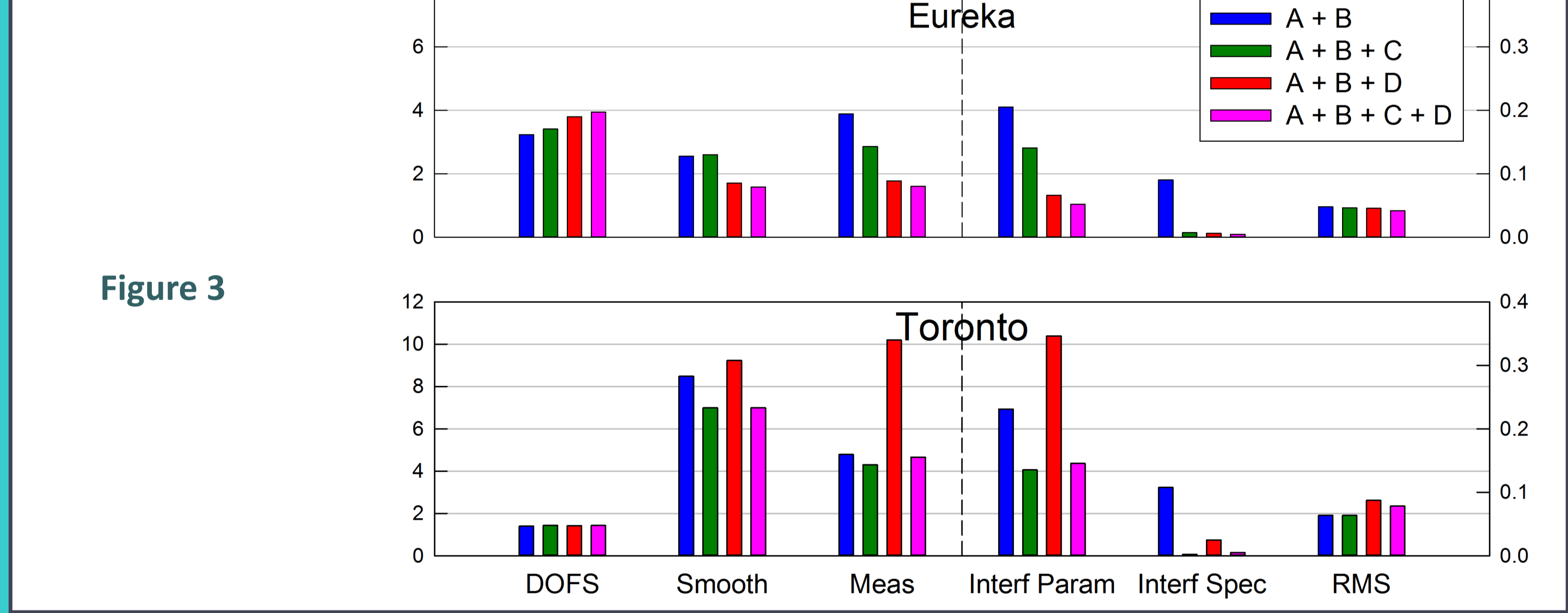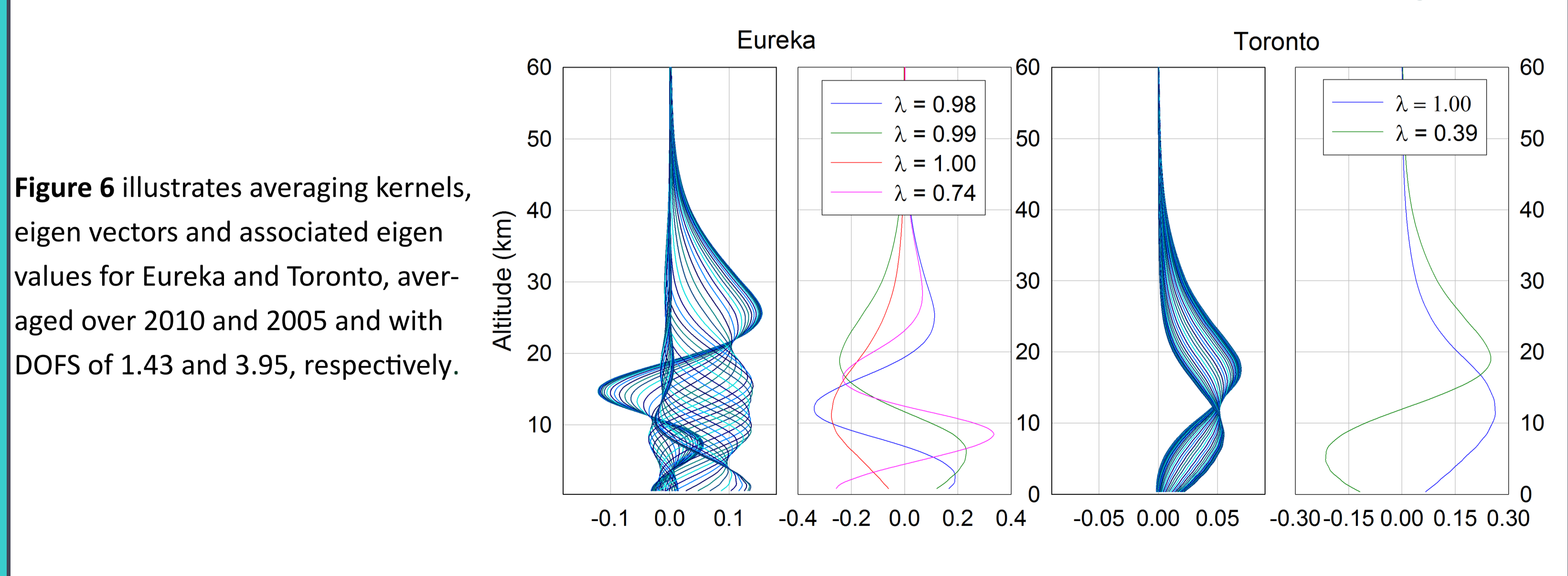

Figure 3

Water vapor interferences

In order to better identify the water vapor interferences, a H_2O specific window (2941.65 –2941.89 cm^{-1}, Bader et al., 2017) is tested as the fifth window. **Figure 4** - Correlation between CH_3D and H_2O retrieved total columns with (in red) and without the use of the "H_2O" window (in green). While combining the 4 windows reduces smoothing and measurement errors and increases DOFS (see Fig. 3), overlapping of H_2O and CH_3D absorption lines in windows **C** and **D** (see Fig. 2), may result in a misinterpretation of the CH_3D total columns for humid days.

Figure 4

Instrumentation & Database

Results presented here (see Figure 5) are from FTIR ground-based observations datasets collected at:

Toronto, ON, Canada (43.7 °N, -79.4 °E, 174 m a.s.l. ; Wiacek, et al., 2007) with a Bomem DA8 Fourier Transform Spectrometer and consists of ~1430 days of solar observations since May 2002.

Eureka, NU, Canada (80.1 °N, -86.4 °E, 610 m a.s.l. ; Batchelor et al., 2009) with a Bruker IFS-125 HR Fourier Transform Spectrometer and consists of ~760 days of solar observations since July 2006.

Error budget and information content

Figure 6

Figure 6 illustrates averaging kernels, eigen vectors and associated eigen values for Eureka and Toronto, averaged over 2010 and 2005 and with DOFS of 1.43 and 3.95, respectively.

Preliminary, unfiltered, time series for Eureka and Toronto

Figure 5

Conclusion & Outlook

The development of a retrieval strategy for CH_3D is challenging as it requires accuracy and precision in order to compute reliable isotopic ratio of atmospheric methane. To this end, the impact of the water vapor interference needs to be properly assessed. The next step of this work is therefore to test this retrieval strategy at additional FTIR observation sites, located at different latitudes such as in the Tropic region or the Southern Hemisphere, allowing us to analyze of a wide range of humidity cases. Those stations include : **Saint-Denis, Réunion Island** (20.9 °S, 55.5 °E, 85 m a.s.l.); **Maido, Réunion Island** (21.1 °S, 55.4 °E, 2155 m a.s.l.); **Portovelho, Brasil** (-8.8 °S, 296.1 °E, 87 m a.s.l), **Lauder, New Zealand** (45.0 °S, 169.7 °E, 370 m a.s.l.).
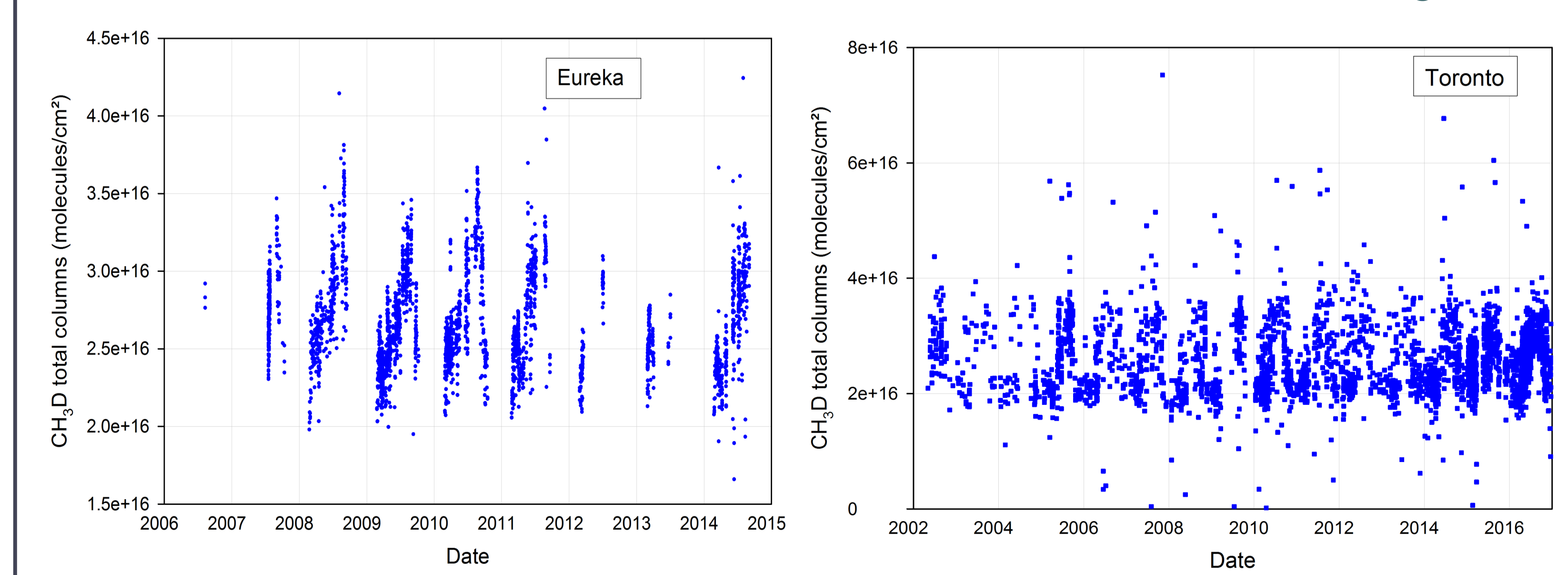
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