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## LETTER

## Evaluating ethane and methane emissions associated with the development of oil and natural gas extraction in North America

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### Abstract

Sharp rises in the atmospheric abundance of ethane ( $C_2H_6$ ) have been detected from 2009 onwards in the Northern Hemisphere as a result of the unprecedented growth in the exploitation of shale gas and tight oil reservoirs in North America. Using time series of  $C_2H_6$  total columns derived from ground-based Fourier transform infrared (FTIR) observations made at five selected Network for the Detection of Atmospheric Composition Change sites, we characterize the recent  $C_2H_6$  evolution and determine growth rates of  $\sim 5\% \text{ yr}^{-1}$  at mid-latitudes and of  $\sim 3\% \text{ yr}^{-1}$  at remote sites. Results from CAM-chem simulations with the Hemispheric Transport of Air Pollutants, Phase II bottom-up inventory for anthropogenic emissions are found to greatly underestimate the current  $C_2H_6$  abundances. Doubling global emissions is required to reconcile the simulations and the observations prior to 2009. We further estimate that North American anthropogenic  $C_2H_6$  emissions have increased from  $1.6 \text{ Tg yr}^{-1}$  in 2008 to  $2.8 \text{ Tg yr}^{-1}$  in 2014, i.e. by 75% over these six years. We also completed a second simulation with new top-down emissions of  $C_2H_6$  from North American oil and gas activities, biofuel consumption and biomass burning, inferred from space-borne observations of methane ( $CH_4$ ) from Greenhouse Gases Observing SATellite. In this simulation, GEOS-Chem is able to reproduce FTIR measurements at the mid-latitudinal sites, underscoring the impact of the North American oil and gas development on the current  $C_2H_6$  abundance. Finally we estimate that the North American oil and gas emissions of  $CH_4$ , a major greenhouse gas, grew from 20 to  $35 \text{ Tg yr}^{-1}$  over the period 2008–2014, in association with the recent  $C_2H_6$  rise.

### 1. Introduction

Ethane ( $C_2H_6$ ) is a ubiquitous constituent of the Earth's atmosphere, with surface concentrations typically ranging from 500 to 2200 ppt over the Northern Hemisphere (Simpson *et al* 2012). As a result of its relatively short lifetime against oxidation by the main tropospheric oxidant, the hydroxyl radical (OH; Rudolph 1995),  $C_2H_6$  presents a significant seasonal modulation, characterized by a winter maximum and a summer minimum. The main  $C_2H_6$  sources are of

anthropogenic origin (62% from leakage during production and transport of natural gas (NG), 20% from biofuel combustion and 18% from biomass burning; e.g., Xiao *et al* 2008), and this produces a strong latitudinal and interhemispheric gradient (Simpson *et al* 2012).

Ethane plays a number of roles in atmospheric chemistry. As the most abundant non-methane volatile organic compound, its oxidation in the presence of nitrogen oxides ( $NO_x$ ) can enhance tropospheric ozone ( $O_3$ ) production, especially in polluted air

masses, and it is a significant source of peroxyacetyl nitrate, the main tropospheric reservoir species for  $\text{NO}_x$  (Fischer *et al* 2014). Ethane directly impacts the oxidizing capacity of the troposphere by serving as an important sink for OH. It also shares important and concurrent anthropogenic emission sources with methane ( $\text{CH}_4$ ), a major greenhouse gas released to the atmosphere by numerous natural processes and human-related activities. A complete understanding of the atmospheric distribution of  $\text{C}_2\text{H}_6$  and any trends in the abundance of this species can be used to better constrain the sources of  $\text{CH}_4$ , in particular from oil and gas activities.

Until very recently, the abundance of  $\text{C}_2\text{H}_6$  in the atmosphere has been declining, and this has been mainly attributed to the reduction of fugitive emissions from its fossil fuel sources (Simpson *et al* 2012) as a result of successful implementation of measures aimed at the reduction of atmospheric pollution. Simpson *et al* (2012) showed that global emissions dropped from 14.3 to 11.3  $\text{Tg yr}^{-1}$  over the period 1984–2010. Several studies have characterized the atmospheric decrease of  $\text{C}_2\text{H}_6$  over the last two decades, and found consistent relative trends in the  $-1$  to  $-2.7\%$   $\text{yr}^{-1}$  range, depending on the site and time period (Franco *et al* 2015, and references therein).

There are multiple lines of evidence that the multi-decade decline in  $\text{C}_2\text{H}_6$  has ended. Using surface measurements of the Photochemical Assessment Monitoring Stations network, Vinciguerra *et al* (2015) showed that  $\text{C}_2\text{H}_6$  mixing ratios increased after 2010 at locations downwind of active wells in North America. Almost simultaneously, Franco *et al* (2015) reported a  $5\%$   $\text{yr}^{-1}$  increase in the total  $\text{C}_2\text{H}_6$  column series after 2009 over the remote high-altitude site of the Jungfraujoch in the Swiss Alps, suggesting that emissions associated with hydraulic fracturing and shale gas operations in North America are affecting Europe.

NG production over the US increased by 40% from 1989 to 2013 (Energy Information Administration, <http://eia.gov/dnav/ng/hist/n9010us2a.htm>). The rate of change of NG production increased in 2006, resulting in an annual production of 835 000 million cubic meters by the year 2013 (figure 1(a)). Gas producing wells are located in many regions of the US, the largest number being located in the northeast and the south central portion of the US (figure 1(b); Energy Information Administration, [https://eia.gov/dnav/ng/ng\\_sum\\_lsum\\_a\\_EPG0\\_xdg\\_count\\_a.htm](https://eia.gov/dnav/ng/ng_sum_lsum_a_EPG0_xdg_count_a.htm)).

Here we use remote-sensing observations from five ground-based Fourier transform infrared (FTIR) instruments over the 2003–2014 time period to characterize the recent  $\text{C}_2\text{H}_6$  abundance increases over North America that we attribute to the intense development of oil and gas extraction in this region. We show that a significant adjustment of the anthropogenic  $\text{C}_2\text{H}_6$  emissions (dominated by the oil and gas sector) available from the most current bottom-up emission inventory is needed to allow a correct

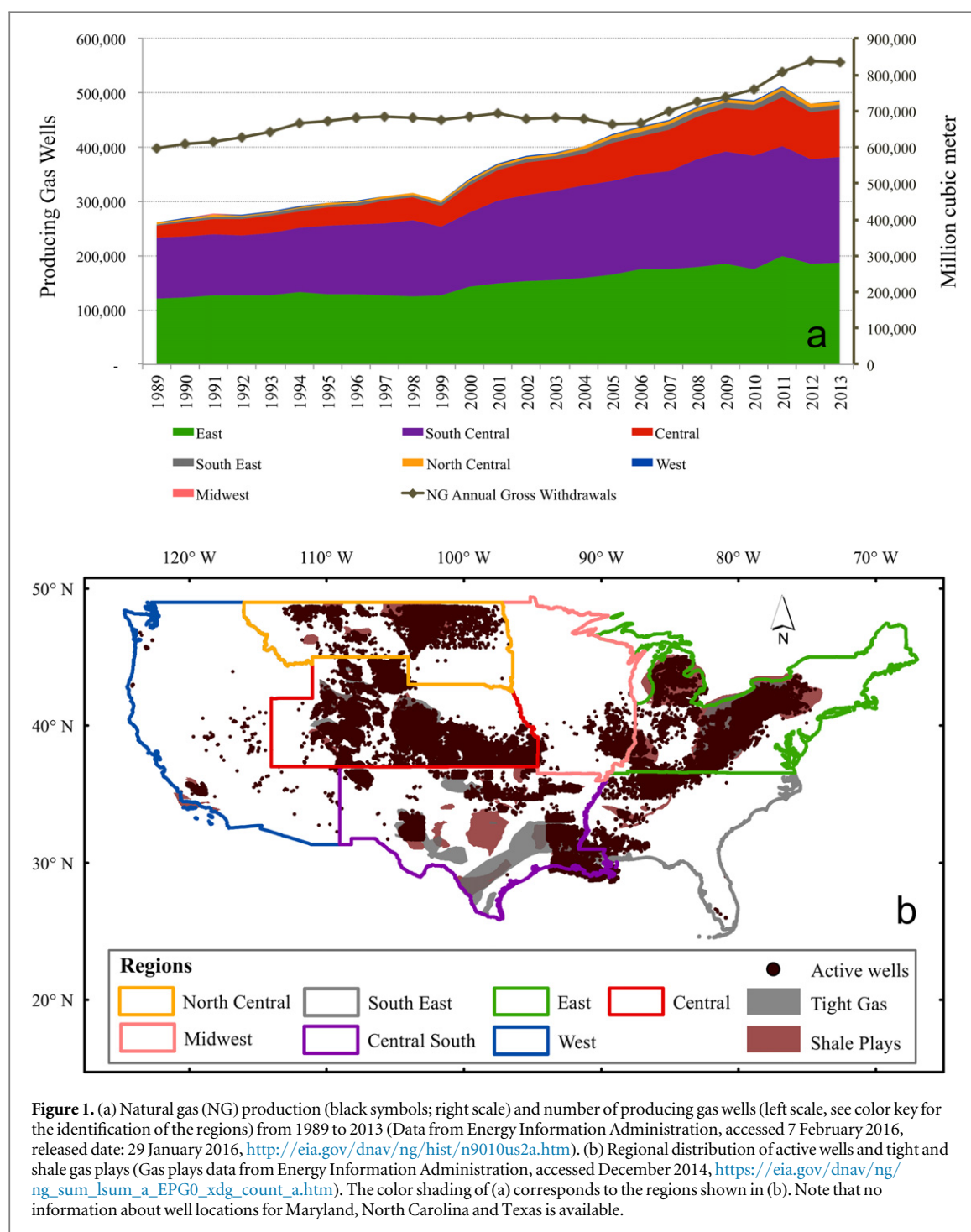
reproduction of the  $\text{C}_2\text{H}_6$  atmospheric levels and recent rise by the CAM-chem model (the Community Atmosphere Model with Chemistry). These findings are confirmed by an independent simulation performed with the chemical transport model GEOS-Chem, implementing spatially resolved top-down emissions of  $\text{C}_2\text{H}_6$  (Turner *et al* 2015).

## 2. Methods

### 2.1. FTIR and portable atmospheric research interferometric spectrometer for the infrared (PARIS-IR)

High-resolution infrared solar absorption spectra encompassing  $\text{C}_2\text{H}_6$  absorption features near  $3.5\ \mu\text{m}$  are regularly recorded under clear-sky conditions at globally distributed ground-based sites within the Network for the Detection of Atmospheric Composition Change (NDACC; see <http://ndacc.org> and [www2.acom.ucar.edu/irwg](http://www2.acom.ucar.edu/irwg)). The present study focuses on observations obtained as part of this monitoring effort in North America, namely at Eureka, Thule and Toronto, and at Mauna Loa. Spectra recorded at Boulder, in operation since 2009 and not affiliated yet to NDACC, have also been included to increase the latitudinal coverage. Table 1 provides information on these sites. To check the ability of lower-resolution, compact and portable instruments to provide meaningful column measurements of  $\text{C}_2\text{H}_6$ , we further considered observations performed by the portable atmospheric research interferometric spectrometer for the infrared (PARIS-IR; Fu *et al* 2007), an instrument based on the design of the atmospheric chemistry experiment-Fourier transform spectrometer (ACE-FTS) in orbit on-board the SCISAT satellite since August 2003 (Bernath *et al* 2005). PARIS-IR has been operated from Eureka each spring since 2006 and from Toronto in 2009 and 2011, side-by-side with the corresponding affiliated NDACC-FTIR spectrometers.

The  $\text{C}_2\text{H}_6$  retrieval strategies used here are consistent with those described in Franco *et al* (2015). In brief, two spectral windows encompassing the  $^{\text{P}}\text{Q}_3$  and  $^{\text{P}}\text{Q}_1$  sub-branches near  $2976$  and  $2983\ \text{cm}^{-1}$  were simultaneously fitted, accounting for interferences by water vapor ( $\text{H}_2\text{O}$ ),  $\text{O}_3$ , methyl chloride ( $\text{CH}_3\text{Cl}$ ) and  $\text{CH}_4$ . The third optional window near  $2986\ \text{cm}^{-1}$ , sometimes affected by water vapor, was used at all sites. The adopted spectroscopic parameters correspond to a combination of HITRAN 2008 for most species (Rothman *et al* 2009), with HITRAN 2012 for  $\text{CH}_3\text{Cl}$  (Rothman *et al* 2013), improved parameters for the  $\text{O}_3$  lines near  $2976.97\ \text{cm}^{-1}$  and a pseudo-linelist for  $\text{C}_2\text{H}_6$  derived from laboratory cross section spectra recorded by Harrison *et al* (2010). Model simulations with the CHemical Atmospheric General Circulation Model for study of atmospheric environment and radiative forcing (CHASER; Sudo *et al* 2002) were used



**Figure 1.** (a) Natural gas (NG) production (black symbols; right scale) and number of producing gas wells (left scale, see color key for the identification of the regions) from 1989 to 2013 (Data from Energy Information Administration, accessed 7 February 2016, released date: 29 January 2016, <http://eia.gov/dnav/ng/hist/n9010us2a.htm>). (b) Regional distribution of active wells and tight and shale gas plays (Gas plays data from Energy Information Administration, accessed December 2014, [https://eia.gov/dnav/ng/ng\\_sum\\_lsum\\_a\\_EPG0\\_xdg\\_count\\_a.htm](https://eia.gov/dnav/ng/ng_sum_lsum_a_EPG0_xdg_count_a.htm)). The color shading of (a) corresponds to the regions shown in (b). Note that no information about well locations for Maryland, North Carolina and Texas is available.

**Table 1.** Information on the FTIR sites with  $C_2H_6$  measurements presented in this study.

FTIR site	Location	Reference
Eureka	Canada, NU, 80.05° N, 86.42° W, 610 m a.s.l.	Batchelor <i>et al</i> (2009)
Thule	Greenland, 76.52° N, 68.77° W, 225 m a.s.l.	Hannigan <i>et al</i> (2009)
Jungfraujoch	Swiss Alps, 46.55° N, 7.98° E, 3580 m a.s.l.	Zander <i>et al</i> (2008)
Toronto	Canada, ON, 43.66° N, 79.40° W, 174 m a.s.l.	Wiacek <i>et al</i> (2007)
Boulder	United States, CO, 40.40° N, 102.50° W, 1612m a.s.l.	
Mauna Loa	United States, HI, 19.54° N, 155.57° W, 3396 m a.s.l.	Hannigan <i>et al</i> (2009)

to build the *a priori* covariance matrix and to determine on a site-by-site basis, a scale factor applied to the v6 climatological *a priori* vertical profiles employed in

the NDACC Infrared Working Group that were derived from the Whole Atmosphere Community Climate Model (WACCM; Garcia *et al* 2007, Eyring

*et al* 2013). The objective characterization of the information content indicated that mean degrees of freedom for signal (DOFS) are in the range of 1.5–1.7 at all sites, providing sensitivity in an altitude range from the ground up to  $\sim 18$  km. The retrieval algorithm and approach adopted for the PARIS-IR low-resolution ( $0.02\text{ cm}^{-1}$ ) observations are consistent with those used for the high-resolution spectra and provide a mean DOFS of approximately 1.0 between the ground and  $\sim 18$  km.

Uncertainties associated with the retrieval of  $\text{C}_2\text{H}_6$  have been evaluated in numerous previous studies (see Franco *et al* 2015 and references therein), for many different sites with a broad range of atmospheric conditions. All concur in estimating a total systematic error on the total columns close to 6%, dominated by the uncertainty affecting the  $\text{C}_2\text{H}_6$  line parameters. Reported random errors are in the 2%–4% range for studies making simultaneous use of several windows, with main contribution by the measurement noise.

## 2.2. CAM-chem

For this study, a simplified version of CAM-chem (Lamarque *et al* 2012), a component of the Community Earth System Model, was used to simulate multi-year distributions of  $\text{C}_2\text{H}_6$  along with tracers of source region contributions. CAM version 4 (CAM4) with bulk aerosols was used at a  $1.9^\circ$  latitude  $\times$   $2.5^\circ$  longitude resolution, with the global OH distribution specified using output from a previous full chemistry simulation for year 2000 (Tilmes *et al* 2015). The meteorology is specified using Modern-Era Retrospective Analysis for Research and Applications meteorological fields corresponding to each year of simulation. The reaction of  $\text{C}_2\text{H}_6$  with OH was the only chemical loss included. Since this version of the model does not include complete chemistry, it will be called CAM- $\text{C}_2\text{H}_6$  throughout this paper.

The initial anthropogenic  $\text{C}_2\text{H}_6$  emissions inventory used with CAM- $\text{C}_2\text{H}_6$  was developed for the Hemispheric Transport of Air Pollutants, Phase II (HTAP2), and is a composite of regional inventories harmonized to represent 2008 and 2010 (Janssens-Maenhout *et al* 2015). Additional  $\text{C}_2\text{H}_6$  emissions included in these simulations are biogenic emissions from the online Model of Emissions of Gases and Aerosols from Nature (MEGAN2.1) biogenic emissions model (Guenther *et al* 2012), and fire emissions from the Fire INventory from NCAR (FINNV1.5; Wiedinmyer *et al* 2011).

Daily mean  $\text{C}_2\text{H}_6$  mixing ratio profiles at the closest pixel to each measurement site were used from the CAM- $\text{C}_2\text{H}_6$  output. To ensure a reliable comparison with the ground-based measurements, we imposed the vertical resolution and sensitivity of the FTIR retrievals to the model outputs before computing the total columns: the individual mixing ratio profiles were re-gridded onto the vertical FTIR layer schemes

and convolved by the averaging kernels (AVKs) according to the formalism of Rodgers and Connor (2003). The re-gridding method is a mass-conservative interpolation, preserving the total  $\text{C}_2\text{H}_6$  mass above the station altitude and ignoring the mass underneath. Seasonally-averaged AVKs were employed for the smoothing.

## 2.3. GEOS-Chem

GEOS-Chem is a chemical transport model driven by assimilated meteorological fields from the Goddard Earth Observing System of the National Aeronautics and Space Administration (NASA) Global Modelling and Assimilation Office (Bey *et al* 2001). Our analysis was based on a  $2^\circ \times 2.5^\circ$  resolution simulation for 2010, with an 18 month spin-up. We used v10-01 with GEOS-5 meteorological fields and the full chemistry ( $\text{NO}_x$ – $\text{O}_x$ –HC–Aer–Br) mechanism. Ethane emission fluxes over the US and Canada were based on  $\text{CH}_4$  fluxes derived from the Greenhouse Gases Observing SATellite (GOSAT) at a  $50\text{ km} \times 50\text{ km}$  spatial resolution (Turner *et al* 2015). The  $\text{CH}_4$  inversions were calculated using a state vector optimally defined with radial basis functions to enable analytical inversion with full error characterization while minimizing aggregation error. A full description of the uncertainty and error characterization of this method for calculating  $\text{CH}_4$  emissions is presented in Turner and Jacob (2015).

In order to attribute nationwide percentages of anthropogenic  $\text{CH}_4$  emissions, Turner *et al* (2015) used prior information on source locations. As a result, they estimated  $\text{CH}_4$  fluxes for 12 anthropogenic categories. In this study, we only considered the categories and thus locations relevant to  $\text{C}_2\text{H}_6$ , and these include: (1) oil and NG, (2) biofuel, and (3) biomass burning. For these categories, we estimated  $\text{C}_2\text{H}_6$  emissions using  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratios from the literature and implemented them into the model using the Harvard-NASA Emissions Component v1.1.005 (Keller *et al* 2014). To estimate oil and gas  $\text{C}_2\text{H}_6$  emission fluxes, we used a single  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratio based on Katzenstein *et al* (2003). To derive biomass burning and biofuel  $\text{C}_2\text{H}_6$  emissions, we considered biofuel consumption as residential biomass burning; and we used the  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratios for temperate forests from Akagi *et al* (2011). The use of relatively few emission ratios is a large source of uncertainty in this analysis on top of errors associated with the GOSAT based  $\text{CH}_4$  fluxes. However, there are relatively few emission ratios available in the published literature, and our approach offers a simple and reproducible implementation in the model. Consistent with the CAM- $\text{C}_2\text{H}_6$  outputs, we used the GEOS-Chem mixing ratio profiles accounting for the FTIR vertical resolution and sensitivity.



### 3. Results

#### 3.1. Observed ethane increase

We investigated  $\text{C}_2\text{H}_6$  time series derived from the ground-based observations to determine the current abundances of  $\text{C}_2\text{H}_6$  as well as its recent evolution over the North American FTIR sites. The FTIR daily mean total columns from January 2003 through December 2014 are shown as gray circles in figure 2, while the light blue triangles correspond to the daily-averaged PARIS-IR measurements at Eureka and Toronto. On each frame, the right  $y$ -axis scale converts the total columns into approximate surface mole fractions. The scale conversion was determined for each site according to the linear regression between the total column abundance and the  $\text{C}_2\text{H}_6$  mole fraction in the lowermost layer of the FTIR retrieval scheme. These regressions are characterized by a coefficient of determination ( $R^2$ ) of at least 0.8.

Differences in  $\text{C}_2\text{H}_6$  abundance present in figure 2 are largely a function of site latitude (Simpson *et al* 2012) and altitude (Gardiner *et al* 2008, Angelbratt *et al* 2011); the bulk of the  $\text{C}_2\text{H}_6$  molecules are found in the lowermost tropospheric layers. The mean column for each site ( $\pm 1\sigma$ ) is as follows:  $1.7 \pm 0.5$  (Eureka; 610 m a.s.l.),  $1.8 \pm 0.6$  (Thule; 225 m a.s.l.),  $2.1 \pm 0.4$  (Toronto; 174 m a.s.l.),  $1.6 \pm 0.5$  (Boulder; 1612 m a.s.l.) and  $0.6 \pm 0.2$  molec  $\text{cm}^{-2}$  (Mauna Loa; 3396 m a.s.l.). There are also seasonal and interannual differences in the  $\text{C}_2\text{H}_6$  burden between the sites. Mainly driven by the rate of reaction with OH, the typical seasonal peak-to-peak amplitude for  $\text{C}_2\text{H}_6$  is on the order of 50% at Boulder and Toronto, and it increases to  $\sim 80\%$  at the remote sites. It is worth noting the good agreement between the PARIS-IR and FTIR total columns above both Eureka and Toronto (figures 2(a) and (c)).

We characterize the recent atmospheric evolution of  $\text{C}_2\text{H}_6$ , considering the daily means, with a statistical bootstrap resampling tool that combines a linear function and a Fourier series accounting for the intra-annual variability of the data sets (Gardiner *et al* 2008). A third-order Fourier series is used to adjust the seasonal variations, except at the Arctic sites, Eureka and Thule, where a second-order fit is appropriate to capture the seasonality over the spring to fall time period (no observations during the polar night). As in Franco *et al* (2015), we consider separately the daily mean subsets before 1 January 2009 (when enough observations are available), and after 1 January 2009. The fitted seasonality is drawn as a blue curve in each frame of figure 2, while the green and red solid lines designate the corresponding linear regressions. At Eureka (figure 2(a)), a linear regression (red dashed line) is calculated solely on the basis of the 2009–2014 PARIS-IR campaign measurements. Figure 3 shows the relative annual  $\text{C}_2\text{H}_6$  rates of change, using either the January 2003 or January 2009 computed total columns as reference. The available annual rates of  $\text{C}_2\text{H}_6$  over

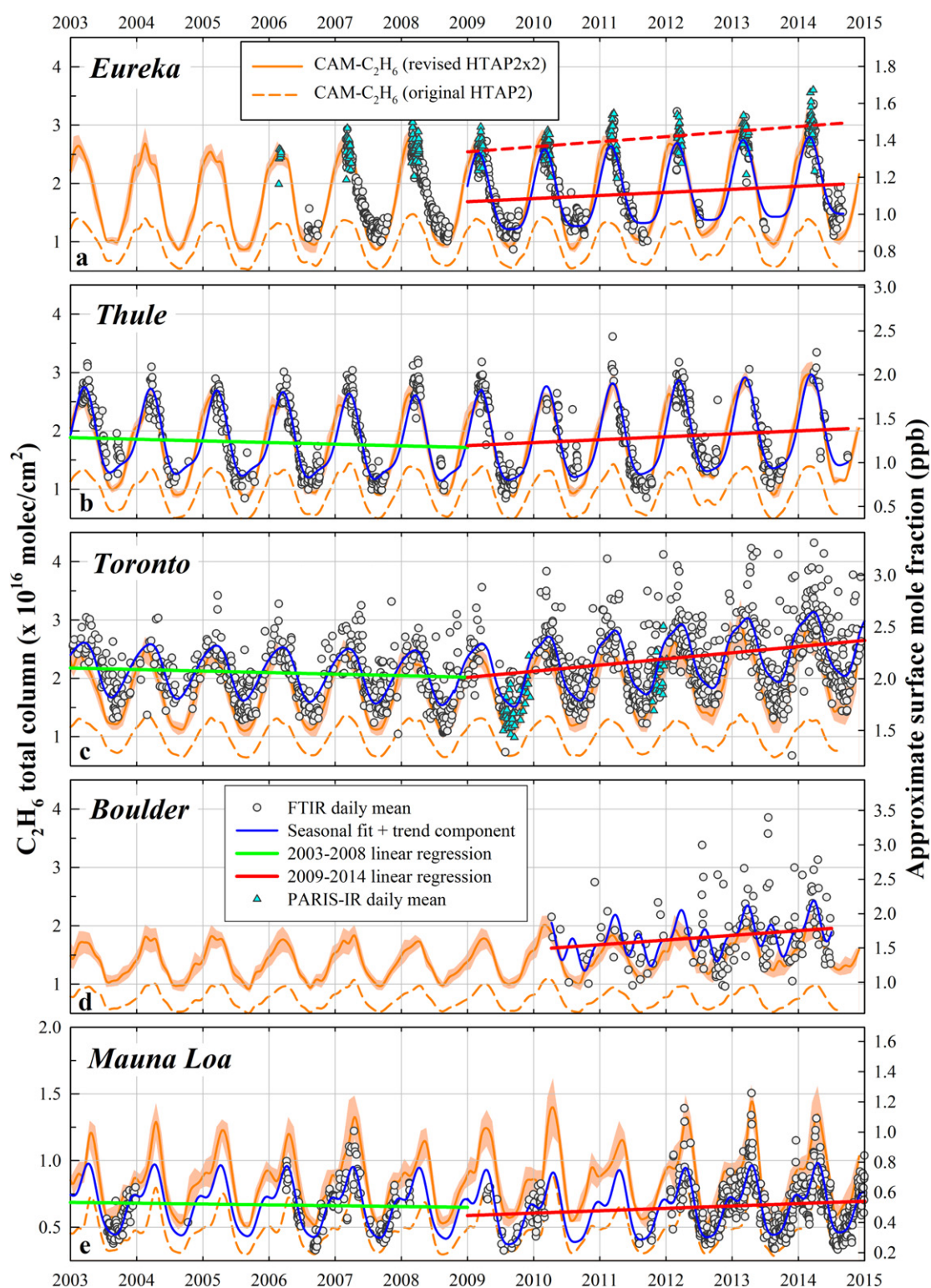
both the 2003–2008 and 2009–2014 time periods, along with the  $2\sigma$  confidence level, for the five FTIR sites are plotted in blue. The equivalent annual rates derived from the Jungfraujoch (table 1) time series investigated in Franco *et al* (2015) are added for comparison.

From 2003 to 2008, we observe a slow decline of the  $\text{C}_2\text{H}_6$  total columns between  $-1.0$  and  $-1.5\%$   $\text{yr}^{-1}$ , with consistent rates within the different latitudes (figure 3(a)). The Mauna Loa rate of change is not significant at the  $2\sigma$  confidence level ( $0.9 \pm 1.1\%$   $\text{yr}^{-1}$ ). However, when using the dataset from inception, we compute a decrease of  $-1.0 \pm 0.3\%$   $\text{yr}^{-1}$  over 1995–2008. These results agree with the global decline of the atmospheric  $\text{C}_2\text{H}_6$  burden from the mid-1980s up to the end of the 2000s, which was widely reported in the scientific literature (e.g., Gardiner *et al* 2008, Angelbratt *et al* 2011, Franco *et al* 2015, and references therein). It was attributed to reduced fugitive fossil fuel emissions that were thought to also contribute significantly to the slowing growth rate of atmospheric  $\text{CH}_4$  since the mid-1980s (Aydin *et al* 2011, Simpson *et al* 2012).

However, as at Jungfraujoch (Franco *et al* 2015), the FTIR measurements over the North American sites show a reversal of the long term decline in  $\text{C}_2\text{H}_6$  around 2009, followed by a sharp and significant (at the  $2\sigma$  confidence level) increase at all FTIR sites (figure 3(b)). The observed rates of change are very consistent and vary between  $\sim 3\%$   $\text{yr}^{-1}$  at the remote stations and  $\sim 5\%$   $\text{yr}^{-1}$  at mid-latitudes. The increase in  $\text{C}_2\text{H}_6$  deduced from the PARIS-IR and FTIR observations at Eureka are very consistent as well. We hypothesize that this recent increase is the result of the recent massive growth in the exploitation of shale gas and tight oil reservoirs in North America, where the drilling productivity began to grow rapidly after 2009 (Schneising *et al* 2014, Warneke *et al* 2014, Vinciguerra *et al* 2015). Of the observation sites presented here, Boulder is located closest to a highly productive oil and gas basin, the Denver-Julesburg Basin. We suggest that is why the Boulder data show a large variability in the  $\text{C}_2\text{H}_6$  columns ( $5.0 \pm 4.5\%$   $\text{yr}^{-1}$ ), influenced by local air mass circulation. Similar elevated mixing ratios of  $\text{C}_2\text{H}_6$  have been observed at the Boulder Atmospheric Observatory by Gilman *et al* (2013).

#### 3.2. Results from HTAP2 emissions inventory

We compared  $\text{C}_2\text{H}_6$  simulations produced with CAM- $\text{C}_2\text{H}_6$  for the period 2003–2014, using the bottom-up anthropogenic inventory HTAP2, with the remote-sensing measurements. The  $\text{C}_2\text{H}_6$  total columns derived from this simulation, represented by the dashed curve in figure 2, greatly underestimate the FTIR observations at all sites in terms of  $\text{C}_2\text{H}_6$  abundance and seasonal amplitude, with a low bias that is far larger than the typical systematic uncertainty

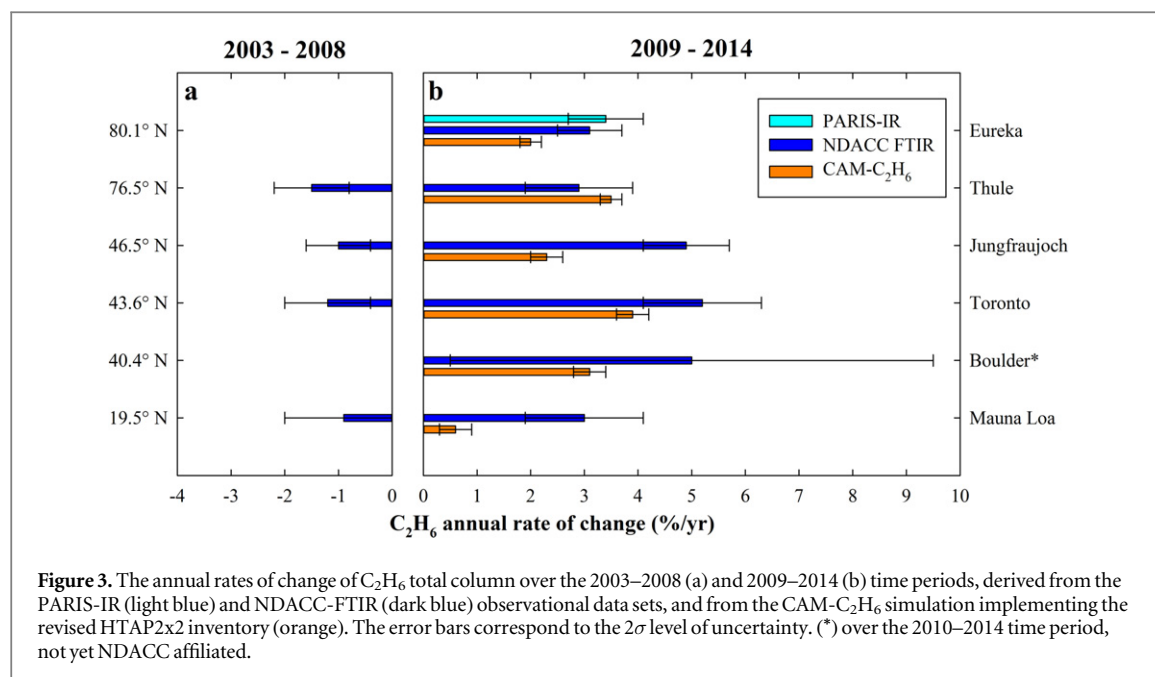


**Figure 2.** Daily mean  $C_2H_6$  total columns derived from the FTIR (gray circles) and PARIS-IR (light blue triangles) observations performed between January 2003 and December 2014. The right y-axis scale converts the total columns into approximate surface mole fraction (see text for details). The blue curve visualizes the function (including seasonal modulation and trend component) fitted to all daily FTIR means over the periods 2003–2008 and 2009–2014, using a bootstrap tool (Gardiner *et al* 2008). The green and red lines are the associated linear regressions (as solid line for FTIR and dashed line for PARIS-IR). The dashed and solid orange curves are the monthly mean  $C_2H_6$  total columns simulated by CAM- $C_2H_6$ , implementing the original HTAP2 and revised HTAP2x2 (with increasing North American emissions) inventories, respectively. The shaded area corresponds to the  $1\sigma$  standard deviation.

of 6% affecting the total columns. Furthermore, the model does not reproduce the recent  $C_2H_6$  increase.

Based on comparisons between the model results and the FTIR measurements, we estimate that the

global HTAP2 anthropogenic  $C_2H_6$  emissions must be doubled to simulate the observed  $C_2H_6$  abundance prior to 2009. We refer to this quantity of  $C_2H_6$  emissions as HTAP2x2. An additional increase in  $C_2H_6$



**Table 2.** Total annual emissions of  $C_2H_6$  (in  $Tg\ yr^{-1}$ ) used for the CAM- $C_2H_6$  (with the original HTAP2 and revised HTAP2x2 inventories) and GEOS-Chem v10-01 simulations, according to regional/sector sources. The original HTAP2 anthropogenic emissions for 2008 are used for all years, while in the revised HTAP2x2 the global anthropogenic emissions for 2008 were doubled for all years prior to 2009, with increasing North American emissions after 2009.

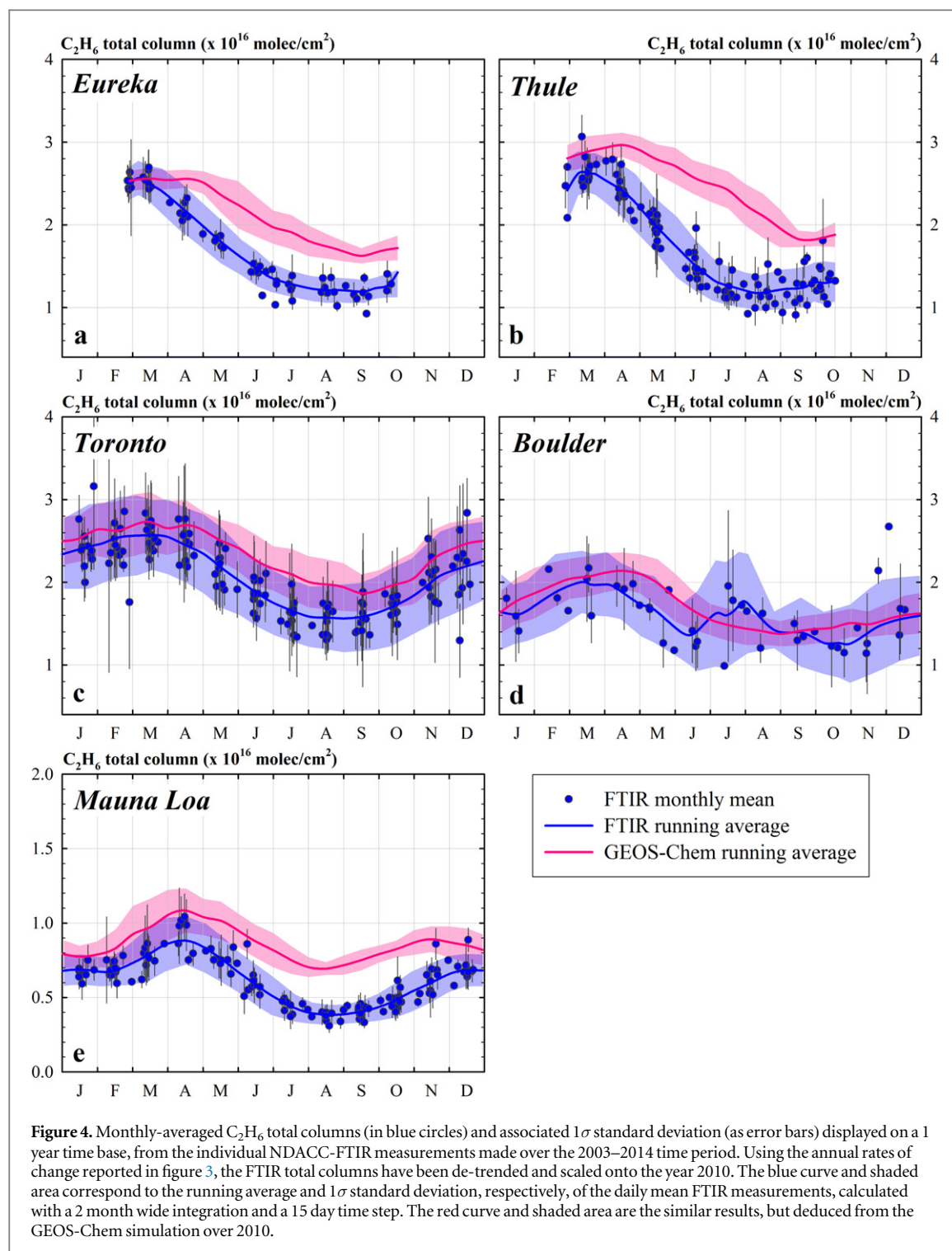
Region—sector	CAM- $C_2H_6$ (original HTAP2)	CAM- $C_2H_6$ (revised HTAP2x2)			GEOS-Chem 2010
		2008–2014	2008	2010	2014
Globe—all sectors	9.7–10.2		17.3	17.9	18.7
Globe—anthropogenic	7.5		15.0	15.3	16.2
Globe—biomass burning	1.8–2.3		1.9	2.2	2.2
Globe—biogenic	0.4		0.4	0.4	0.4
North America—anthropogenic	0.8		1.6	1.9	2.8

emissions beyond HTAP2x2 is required to simulate the recent rise from 2009 to 2014. Given that  $C_2H_6$  emissions related to the oil and gas sector represent up to 80% of the total anthropogenic  $C_2H_6$  emissions over North America, and if we assume that the missing emissions during this period resulted from the recent increase in oil and gas extraction in North America, we can use the model to estimate the increase in  $C_2H_6$  emissions needed to match the observations. To match the 2014 observations at the continental sites, the North American annual contribution has to almost double over the period 2009–2014. This corresponds to a 1.2 Tg increase of the North American annual  $C_2H_6$  emissions in 2014 over the 2008 emission rates. An overview of the total  $C_2H_6$  emission rates used for the CAM- $C_2H_6$  simulations is provided in table 2.

The solid orange line in figure 2 signifies the  $C_2H_6$  total columns simulated by CAM- $C_2H_6$  with the revised HTAP2x2 inventory and North American emission increases from 2009 onwards. Similar to the FTIR time series, the annual rates of change relative to January 2009 derived from this new CAM- $C_2H_6$

simulation are calculated and reported in figure 3. The results show a better agreement with the remote-sensing time series for both the abundance of  $C_2H_6$  and its seasonal amplitude, especially at the northern sites. The mean daily biases of the model to the FTIR fitted seasonality over the period 2009–2014 are as follows:  $-4 \pm 16\%$  (Eureka),  $-4 \pm 14\%$  (Thule),  $-18 \pm 13\%$  (Toronto),  $-15 \pm 15\%$  (Boulder) and  $+37 \pm 18\%$  (Mauna Loa). Globally, the revised HTAP2x2 inventory allows the model to simulate significant  $C_2H_6$  increases between  $\sim 2.5$  and  $\sim 4\%$   $yr^{-1}$  from 2009 onwards, although the model still slightly underestimates the rates of change observed at mid-latitudes. Similar findings are deduced from the comparison between CAM- $C_2H_6$  and FTIR at Jungfraujoch. These results support the hypothesis that the enhanced North American oil and gas extraction largely contributes to the recent  $C_2H_6$  increase detected, as assumed previously by Franco *et al* (2015). For the remote non-continental Mauna Loa site, the CAM- $C_2H_6$  results overestimate the FTIR data (figure 2(e)), suggesting that the emissions in Asia (more directly





**Figure 4.** Monthly-averaged  $C_2H_6$  total columns (in blue circles) and associated  $1\sigma$  standard deviation (as error bars) displayed on a 1 year time base, from the individual NDACC-FTIR measurements made over the 2003–2014 time period. Using the annual rates of change reported in figure 3, the FTIR total columns have been de-trended and scaled onto the year 2010. The blue curve and shaded area correspond to the running average and  $1\sigma$  standard deviation, respectively, of the daily mean FTIR measurements, calculated with a 2 month wide integration and a 15 day time step. The red curve and shaded area are the similar results, but deduced from the GEOS-Chem simulation over 2010.

upwind of Mauna Loa) should not be increased as much as 2 times the original HTAP2 inventory.

### 3.3. Results from GOSAT-based inventory

In this section, we compare the results of GEOS-Chem simulations performed with a new top-down inventory of anthropogenic  $C_2H_6$  emissions, based on  $CH_4$  measurements from GOSAT, to the FTIR observations. Since this new inventory is only for 2010, we compare the simulated  $C_2H_6$  columns to the FTIR measurements for this year only (figure 4). In order to

provide more robust statistics for the representation of the  $C_2H_6$  seasonal cycle at each site, the available daily mean columns from the 2003–2014 FTIR time series are de-trended and scaled to the year 2010 according to the annual rates of change reported in figure 3. In figure 4, the FTIR monthly means are represented as blue circles along with  $1\sigma$  standard deviation as error bars, while the blue curve and the shaded area correspond to the running average of the daily mean total columns (with a 2 month wide integration and a 15 day time step) and the associated  $1\sigma$  standard



deviation, respectively. Similarly, the red curve and shaded area designate the GEOS-Chem results. The total  $C_2H_6$  emissions provided from the top-down inventory for the year 2010 are reported in table 2.

GEOS-Chem properly simulates the late winter maximum abundance of  $C_2H_6$  (figure 4) and reproduces the FTIR total columns found at the two mid-latitude sites, Toronto and Boulder (figures 4(c) and (d)). Both stations are located in the vicinity of intense oil and NG basins: several studies have shown a volatile organic compound source signature associated with the oil and gas industry near Boulder (Pétron *et al* 2012, Gilman *et al* 2013, Swarthout *et al* 2013, Thompson *et al* 2014), while Toronto is located north of one of the most active basins in the US, the Marcellus shale gas play. Due to its relatively coarse horizontal resolution, the model dilutes local enhancements in  $C_2H_6$  and hence does not simulate the secondary maximum observed at Boulder during summertime (which is likely due to local air mass circulations).

GEOS-Chem shows a high-bias for the summertime  $C_2H_6$  total columns at most sites, especially the remote sites (Eureka, Thule and Mauna Loa). The levels of OH, the main tropospheric sink of  $C_2H_6$ , are globally lower by  $\sim 10\%$ – $15\%$  in GEOS-Chem v10-01 with respect to previous model versions. This leads to less  $C_2H_6$  oxidation at the time of OH maximum and to an underestimation of the seasonal cycle. This is particularly relevant for the polar sites, where the lower insolation dampens further the photochemical oxidation, causing  $C_2H_6$  to accumulate in summer. We cannot rule out a contribution from transport; however, direct transport of pollutants into the arctic is less frequent during summer (Klonecki *et al* 2003).

The assumptions with regard to the  $C_2H_6/CH_4$  ratios could also induce uncertainties in the inferred  $C_2H_6$  emissions and could contribute to the biases observed between GEOS-Chem and some FTIR results. Indeed, such ratios largely vary in space and time, e.g., according to the types of facilities and the composition of the NG (Mitchel *et al* 2015, Subramanian *et al* 2015).

#### 4. Discussion and conclusions

We used NDACC-FTIR and PARIS-IR time series from five sites to characterize the recent changes in the abundance of  $C_2H_6$  over North America, and we determined significant annual growth rates of  $3\%$ – $5\%$   $yr^{-1}$  over 2009–2014, depending on the latitude. These results corroborate the increase observed in the European remote atmosphere and attributed to the development of oil and NG extraction in North America (Franco *et al* 2015). Using customized simulations of CAM-chem, we evaluated the magnitude of the anthropogenic  $C_2H_6$  emissions required to simulate the observed abundance of  $C_2H_6$  prior to

2009 and its subsequent rise. First the simulations indicate that a doubling of the global HTAP2 anthropogenic emissions is necessary to match the  $C_2H_6$  measurements prior to 2009. Furthermore, an additional increase of the North American anthropogenic  $C_2H_6$  emissions-dominated by up to 80% by emissions from the oil and gas sector—from  $1.6\text{ Tg yr}^{-1}$  in 2008 to  $2.8\text{ Tg yr}^{-1}$  in 2014, i.e. by 75%, is needed to capture the recent  $C_2H_6$  atmospheric rise. In an upcoming analysis, it is our aim to refine the source attribution and identification of the geographical origin of the missing emissions with the help of  $C_2H_6$ -tagged simulations and more than twenty NDACC-FTIR time series from various locations around the globe.

Simulations of GEOS-Chem v10-01 were run using  $C_2H_6$  emissions over North America derived from space-borne  $CH_4$  observations from GOSAT (Turner *et al* 2015). By using a single  $C_2H_6/CH_4$  emission ratio for each source category, we estimated  $C_2H_6$  emissions from oil and gas activities, biofuel consumption and biomass burning. Results from GEOS-Chem implementing this new top-down inventory agreed well with the FTIR measurements at the mid-latitudinal sites, close to regions with high drilling productivity, but overestimated the summertime minimum at remote sites. These independent results contribute to underscoring the impact of large emissions associated with hydraulic fracturing and shale gas operations in North America on the enhanced  $C_2H_6$  abundance in the atmosphere. It is worth noting the good agreement between the emission rates derived for the year 2010 from the CAM- $C_2H_6$  and GEOS-Chem model investigations (table 2), with the top-down approach offering the opportunity to allocate the  $C_2H_6$  emissions on the basis of measurements, for a more accurate representation of recent changes in the atmospheric composition.

Ethane shares important anthropogenic sources with  $CH_4$ , the second most important anthropogenic greenhouse gas, of which the growth rate in the atmosphere has gone on the rise again since the mid-2000s (e.g., Kirschke *et al* 2013, Nisbet *et al* 2014). Using  $C_2H_6$  as a proxy can help to constrain the budget of  $CH_4$  for the emissions originating from the recent massive growth in the North American oil and gas industries. If we apply the  $C_2H_6/CH_4$  ratios used to derive the  $C_2H_6$  emissions from the GOSAT measurements, we estimate that the  $CH_4$  emissions from oil and gas activities in North America have increased from  $20\text{ Tg yr}^{-1}$  in 2008 to  $35\text{ Tg yr}^{-1}$  in 2014, in association with the recent rise of the annual  $C_2H_6$  emissions.

Pursuing atmospheric monitoring activities is of primary importance for evaluating the impacts of the exploitation of shale gas and tight oil reservoirs on greenhouse gas emissions and air quality degradation, especially now that many countries worldwide, e.g., in Europe, are investigating the possibility of starting

shale gas exploitation within their own territory in the near future.

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