

## RESEARCH ARTICLE

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## Key Points:

- We present a global  $C_2H_6$  emission inventory and simulate  $C_2H_6$  abundances for the year 2010 by using the GEOS-Chem model
- Northern Hemisphere fossil fuel sources represent 95% of global fossil fuel emissions and half of total global  $C_2H_6$  emissions
- NEI 2011  $C_2H_6$  emissions produce  $C_2H_6$  mixing ratios that are 14–50% of those observed by recent aircraft observations across the U.S.

## Supporting Information:

- Supporting Information S1

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## Revisiting global fossil fuel and biofuel emissions of ethane

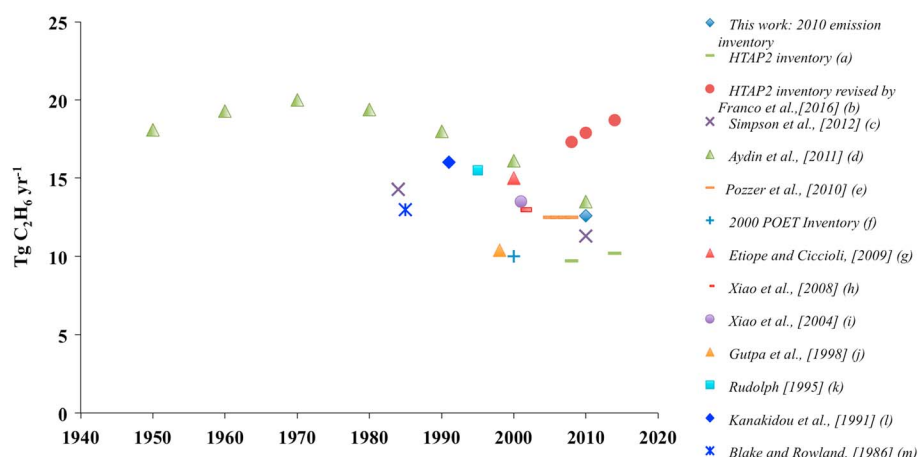
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**Abstract** Recent measurements over the Northern Hemisphere indicate that the long-term decline in the atmospheric burden of ethane ( $C_2H_6$ ) has ended and the abundance increased dramatically between 2010 and 2014. The rise in  $C_2H_6$  atmospheric abundances has been attributed to oil and natural gas extraction in North America. Existing global  $C_2H_6$  emission inventories are based on outdated activity maps that do not account for current oil and natural gas exploitation regions. We present an updated global  $C_2H_6$  emission inventory based on 2010 satellite-derived  $CH_4$  fluxes with adjusted  $C_2H_6$  emissions over the U.S. from the National Emission Inventory (NEI 2011). We contrast our global 2010  $C_2H_6$  emission inventory with one developed for 2001. The  $C_2H_6$  difference between global anthropogenic emissions is subtle (7.9 versus  $7.2 \text{ Tg yr}^{-1}$ ), but the spatial distribution of the emissions is distinct. In the 2010  $C_2H_6$  inventory, fossil fuel sources in the Northern Hemisphere represent half of global  $C_2H_6$  emissions and 95% of global fossil fuel emissions. Over the U.S., unadjusted NEI 2011  $C_2H_6$  emissions produce mixing ratios that are 14–50% of those observed by aircraft observations (2008–2014). When the NEI 2011  $C_2H_6$  emission totals are scaled by a factor of 1.4, the Goddard Earth Observing System Chem model largely reproduces a regional suite of observations, with the exception of the central U.S., where it continues to underpredict observed mixing ratios in the lower troposphere. We estimate monthly mean contributions of fossil fuel  $C_2H_6$  emissions to ozone and peroxyacetyl nitrate surface mixing ratios over North America of ~1% and ~8%, respectively.

## 1. Introduction

Ethane ( $C_2H_6$ ) is a hydrocarbon emitted mainly during the production, processing, and transportation of natural gas, and it has been proposed as a tracer for fugitive emissions from natural gas production [Schwartz et al., 2014; Swarthout et al., 2013; Vinciguerra et al., 2015]. In locations with multiple methane ( $CH_4$ ) sources (e.g., cows, oil and gas, rice production, and wetlands),  $C_2H_6$  can be used as a tracer for fossil fuel  $CH_4$  emissions [McKain et al., 2015; Roscioli et al., 2015]. Natural gas leakage contributes about ~60% of  $C_2H_6$  emissions globally [Xiao et al., 2008] and up to 70% in regions with active oil and gas development [Gilman et al., 2013]. Other important sources of  $C_2H_6$  are biomass burning and biofuel consumption (domestic wood fuels), and each of these sources is estimated to individually account for ~20% of global emissions [Rudolph and Ehhalt, 1981; Singh and Zimmerman, 1992; Xiao et al., 2008; Zimmerman et al., 1988]. Biogenic and oceanic emissions of  $C_2H_6$  are considered negligible on a global scale [Plass-Dülmer et al., 1995; Rudolph, 1995; Zimmerman et al., 1988].

Ethane is one of the most abundant volatile organic compounds (VOCs) in the atmosphere after  $CH_4$ . Observed  $C_2H_6$  mixing ratios near the surface range from ~0.2 ppbv over remote regions of the Southern Hemisphere [Wofsy et al., 2012] and up to 1500 ppbv over oil and natural gas basins [Gilman et al., 2013; Helmig et al., 2014b; Thompson et al., 2014]. The primary tropospheric sink of  $C_2H_6$  is oxidation via reaction with hydroxyl radicals (OH). This loss pathway gives atmospheric  $C_2H_6$  a strong seasonality and a seasonally dependent lifetime with a global annual average of ~2 months [Rudolph and Ehhalt, 1981]. Based upon an



**Figure 1.** Estimated global annual emissions of  $C_2H_6$  in  $Tg\ yr^{-1}$ . Total emissions correspond to the base year of each global estimate, if any, otherwise they correspond to the year they were published. (a) HTAP2 inventory for 2008 and 2014 as reported by Franco *et al.* [2016]. Total emissions from anthropogenic sources ( $7.5\ Tg\ yr^{-1}$ ), biomass burning ( $1.8\text{--}2.3\ Tg\ yr^{-1}$ ), and biogenic ( $0.4\ Tg\ yr^{-1}$ ). (b) HTAP2 global anthropogenic emissions for 2008 were doubled for all years prior to 2009, with increasing North American emissions after 2009. (c) Total emissions from fossil fuels ( $8.0\text{--}9.2\ Tg\ yr^{-1}$ ), biofuels ( $2.6\ Tg\ yr^{-1}$ ), and biomass burning ( $2.4\text{--}2.8\ Tg\ yr^{-1}$ ). (d) Emissions histories of total emissions from fossil fuels, biofuels and biomass burning. (e) Total emissions from anthropogenic ( $9.2\ Tg\ yr^{-1}$ ), biomass burning ( $2.8\ Tg\ yr^{-1}$ ), and oceanic ( $0.5\ Tg\ yr^{-1}$ ) sources. (f) POET inventory for 2000 as reported by Etiope and Ciccioli [2009]. Total emissions from anthropogenic ( $5.7\ Tg\ yr^{-1}$ ), forest-savanna burning ( $2.6\ Tg\ yr^{-1}$ ), biogenic ( $0.8\ Tg\ yr^{-1}$ ), and ocean ( $0.8\ Tg\ yr^{-1}$ ). (g) Total emissions from POET Inventory base year 2000, with additional geologic emissions ( $2\text{--}4\ Tg\ yr^{-1}$ ). (h) Total emissions from fossil fuels ( $8.0\ Tg\ yr^{-1}$ ), biofuels ( $2.6\ Tg\ yr^{-1}$ ), and biomass burning ( $2.4\ Tg\ yr^{-1}$ ). (i) Total emissions reported by Xiao *et al.* [2008]. (j) As reported by Gupta *et al.* [1998]. (k) As reported by Rudolph [1995]. (l) As reported by Kanakidou *et al.* [1991]. (m) As reported by Blake and Rowland [1986].

approximate  $CH_4/C_2H_6$  ratio of 2000 ppbv/2 ppbv and their relative reaction rates with OH,  $C_2H_6$  can make an instantaneous contribution of 4–7% of the total OH loss for these two species combined (depending upon temperature and the specific enhancements encountered). Strong increases in  $C_2H_6$  relative to  $CH_4$  have been found in shale gas-producing areas such as the Bakken [Kort *et al.*, 2016], and thus, the contribution of  $C_2H_6$  to OH reactivity may become more important in the future. Other minor tropospheric sinks of  $C_2H_6$  include reaction with chlorine (Cl) radicals [Aikin *et al.*, 1982] and loss via transport into the stratosphere [Rudolph, 1995]. The relatively long lifetime of  $C_2H_6$  allows it to be subject to long-range transport and to be relatively well mixed in the troposphere within each hemisphere. Since most of the anthropogenic  $C_2H_6$  sources are concentrated in the Northern Hemisphere, and its lifetime is shorter than the interhemispheric exchange rate, there is a strong hemispheric gradient in  $C_2H_6$  [Aydin *et al.*, 2011; Helmig *et al.*, 2016; Pozzer *et al.*, 2010; Rudolph, 1995; Simpson *et al.*, 2012].

Ethane is a precursor of carbon monoxide (CO), ozone ( $O_3$ ), and peroxyacetyl nitrate (PAN) in the troposphere [Aikin *et al.*, 1982].  $C_2H_6$  degradation can lead to the production of  $O_3$  via two pathways: (1)  $C_2H_6$  oxidation by OH radicals in the presence of nitrogen oxide radicals ( $NO_x = NO + NO_2$ ) and (2) by serving as a precursor for PAN. PAN acts as a reservoir for  $NO_x$  [Aikin *et al.*, 1982; Fischer *et al.*, 2014], and its thermal decomposition over remote areas can efficiently produce  $O_3$  [Fischer *et al.*, 2011].  $C_2H_6$  impacts the distribution of several atmospherically relevant species due to its main removal process via reaction with OH radicals [Blake and Rowland, 1986]; however, this impact is smaller compared to other species such as CO,  $CH_4$ , and isoprene.

Global  $C_2H_6$  emissions have significantly changed over the last century. The recent literature is summarized in Figure 1. Briefly, measurements in firn air from Greenland and Antarctica show rising concentrations of  $C_2H_6$  starting in the 1900s and peaking in the 1970s, followed by a decrease that lasted until the late 2000s [Aydin *et al.*, 2011; Helmig *et al.*, 2014a]. The decrease in  $C_2H_6$  between 1970 and 2006 observed by Aydin *et al.* [2011] was attributed to a reduction in fugitive emissions from the fossil fuel sector. Simpson *et al.* [2012] observed the same decreasing trend from surface flask measurements and found a strong correlation between global average  $C_2H_6$  mixing ratios and  $CH_4$  growth rates from 1985 to 2010, suggesting that these light alkanes have a common source.

There is evidence that the long-term decline in  $C_2H_6$  in the Northern Hemisphere recently reversed [Franco *et al.*, 2015; Helmig *et al.*, 2014a]. The change is postulated to be due to increased emissions tied to the recent growth of shale gas exploration and development in the U.S. [Franco *et al.*, 2016; Helmig *et al.*, 2016]. Helmig *et al.* [2016] estimate a mean  $C_2H_6$  annual emission increase of  $0.42 \pm 0.19 \text{ Tg yr}^{-1}$  between 2009 and 2014 in the Northern Hemisphere, corresponding to an overall  $2.1 \pm 1.0 \text{ Tg yr}^{-1}$  increase of  $C_2H_6$  emissions for the same period. Franco *et al.* [2015] report a sharp increase ( $4.90 \pm 0.91\% \text{ yr}^{-1}$ ) in measurements of  $C_2H_6$  columns ( $\text{molecules cm}^{-2}$ ) over the Jungfraujoch site in the Swiss Alps between 2009 and 2014. Vinciguerra *et al.* [2015] also showed a  $\sim 25\%$  increase (1.1 ppbv) in hourly mean  $C_2H_6$  surface mixing ratios from 2004 to 2013 at different sites downwind of the Marcellus shale play, one of the largest natural gas producing regions in the U.S. Several recent field measurement campaigns over U.S. natural gas basins have reported very high average mixing ratios of  $C_2H_6$  (up to  $300 \pm 169 \text{ ppbv}$  ( $1\sigma$ ) [Koss *et al.*, 2015]), along with other volatile organic compounds (VOCs) [Gilman *et al.*, 2013; Helmig *et al.*, 2014b; Katzenstein *et al.*, 2003; Pekney *et al.*, 2014; Pétron *et al.*, 2012; Swarthout *et al.*, 2013; Thompson *et al.*, 2014], and several studies have found that  $C_2H_6$  is the quantitatively largest nonmethane VOC emitted during oil and natural gas exploitation [Field *et al.*, 2015; Kort *et al.*, 2016; Vinciguerra *et al.*, 2015; Warneke *et al.*, 2014].

Xiao *et al.* [2008] presented a 2001 global budget for  $C_2H_6$  based on  $CH_4$  emission estimates. They considered the geographical distributions of natural gas production based on production statistics and locations of major oil and gas wells compiled by Fung *et al.* [1991] and compared their results to a suite of observations collected prior to 2004. Therefore, this inventory is expected to be outdated, at least for North America, where the majority of the oil and gas development has occurred since 2004. Although we do not focus on it here, the Hemispheric Transport of Air Pollutants Phase II (HTAP2) is also likely outdated as it requires annual additional 1.2 Tg  $C_2H_6$  emissions from North American sources in 2014 over 2008 emission rates to match  $C_2H_6$  column observations [Franco *et al.*, 2016]. Note that Franco *et al.* [2016] applied that scaling uniformly without focusing on particular geographic regions.

The apparent dynamic nature of  $C_2H_6$  concentrations and the plausible use  $C_2H_6$  as a tracer for  $CH_4$  leakage from the fossil fuel industry serve as motivation for this work. In this study, we present a 2010  $C_2H_6$  emission inventory (beginning of the increasing trend in the abundance of  $C_2H_6$  reported by Franco *et al.* [2015]) and evaluate the differences between this and a previous 2001  $C_2H_6$  global emission inventory. To estimate  $C_2H_6$  emissions for the year 2010 outside the U.S., we use a similar approach to Xiao *et al.* [2008], but based on  $CH_4$  emissions derived from 2010 spaceborne  $CH_4$  observations from the Greenhouse Gases Observing SATellite (GOSAT), and we combined this with adjusted  $C_2H_6$  emissions from the most recent bottom-up U.S. National Emission Inventory (NEI 2011). We implement the emission inventories into the Goddard Earth Observing System (GEOS) Chem chemical transport model and compare the  $C_2H_6$  simulation to a global suite of surface air observations, column measurements, and aircraft profiles.

## 2. Methodology

### 2.1. GEOS-Chem Model Description and Configuration

We use the 3-D chemical transport model GEOS-Chem version 10-01 with tropospheric chemistry driven by GEOS 5 assimilated meteorological fields, from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office [Bey *et al.*, 2001]. This model version includes the Harvard-NASA Emissions Component (HEMCO) version 1.1.005. HEMCO is a stand-alone software component for computing emissions from different sources, regions, and species on a user-defined grid that gives the user the opportunity to combine, overlay, and update a set of data inventories and scale factors [Keller *et al.*, 2014]. Our analysis is based on a  $2^\circ \times 2.5^\circ$  resolution simulation for 2010, with an 18 month spin-up. The GEOS-Chem  $NO_x$ - $O_3$ -HC-Aer-Br chemistry mechanism includes tropospheric  $C_2H_6$  loss via reaction with OH, Br, and  $NO_3$ , with rate constants of  $7.66 \times 10^{-12} \exp(-1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Sander *et al.*, 2011],  $2.36 \times 10^{-10} \exp(-6411/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Parrella *et al.*, 2012], and  $1.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The reaction rate with  $NO_3$  is slow and is considered unimportant for the lifetime of  $C_2H_6$  [Atkinson, 1991; Atkinson *et al.*, 2004; Calvert *et al.*, 2008]. Stratospheric removal of  $C_2H_6$  by Cl is not considered in our simulation, since past studies have estimated it to account for only  $\sim 2\%$  of total global loss [Gupta *et al.*, 1998]. The annual mass-weighted mean OH concentration of  $8.5 \times 10^5 \text{ molecules cm}^{-3}$  in our GEOS-Chem simulation yields a global tropospheric ( $>100 \text{ hPa}$ ) annual mean lifetime for  $C_2H_6$  of  $\sim 93$  days. In the boundary layer ( $>868 \text{ hPa}$ ), we

estimated averaged lifetimes of 67 days globally, 41 days over the tropics (23°N–23°S), and 105 days in the middle-to-high latitudes (23°–66°N, 23°–66°S). Based on the analysis in *Naik et al.* [2013] for other models, our global mean OH abundance of  $8.5 \times 10^5$  molecules  $\text{cm}^{-3}$  would approximately produce  $\text{CH}_4$  and methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) lifetimes of  $\sim 11.6$  and  $\sim 6.7$  years, respectively. Both lifetime values are consistent with observation-derived lifetime estimates from *Prinn et al.* [2005] and *Prather et al.* [2012] which range from 10.2 to 11.2 years for  $\text{CH}_4$  and 6.0 to 6.3 years for  $\text{CH}_3\text{CCl}_3$ .

The public release version of GEOS-Chem v10-01 (used here) does not include tropospheric halogens other than Br, and this is a source of uncertainty in the following analysis. Although prior studies have shown Cl to be a minor sink for  $\text{C}_2\text{H}_6$  [*Gupta et al.*, 1998], in a very recent paper, *Sherwen et al.* [2016] conclude that Cl may be an important  $\text{C}_2\text{H}_6$  sink that can decrease the simulated global burden of  $\text{C}_2\text{H}_6$  by about  $\sim 20\%$ . The lifetime of  $\text{C}_2\text{H}_6$  is very sensitive to simulated OH, and thus, the interpretation of model-measurement comparisons is always limited by our ability to adequately represent the emissions of other trace gases that compete for reaction with OH.

We use Global Fire Emissions Database Version 3 (GFED3) biomass-burning emissions of  $\text{C}_2\text{H}_6$  in the simulation by using both anthropogenic  $\text{C}_2\text{H}_6$  emission inventories [*van der Werf et al.*, 2010]. The GFED3 emission inventory is based on global satellite-derived burned area information from the Moderate Resolution Imaging Spectroradiometer sensor. At a global scale, the estimated uncertainty for biomass burning carbon emissions is around 20% [*van der Werf et al.*, 2010]. GFED3 does not account for many small fires; this may be particularly relevant in the southeastern U.S. during time periods or locations with significant agricultural/prescribed burning [*Randerson et al.*, 2012]. There is interannual variability in the emissions of  $\text{C}_2\text{H}_6$  from fires globally and over the U.S. (23–50°N,  $-130$  to  $60^\circ\text{W}$ ). We compared emissions during 11 years (2001–2010) and found that averaged biomass burning  $\text{C}_2\text{H}_6$  emissions from GFED3 are  $2.1 \pm 0.35$  ( $1\sigma$ ) Tg/yr and  $0.011 \pm 0.0049$  ( $1\sigma$ ) Tg/yr globally and over the U.S., respectively. During 2001–2011, global  $\text{C}_2\text{H}_6$  emissions from biomass burning were highest in 2010; however, over the U.S.,  $\text{C}_2\text{H}_6$  emissions were equal to the average emissions for this period.

A detailed description of fossil fuel and biofuel  $\text{C}_2\text{H}_6$  emissions in our simulations is discussed in section 2.3.3. For emissions of other species such as CO, NO,  $\text{SO}_x$ , and other VOCs, we use global emission inventories (HTAP2 and Emissions Database for Global Atmospheric Research inventory version 4.2 (EDGAR v4.2)) overwritten by available regional emission inventories for Asia, Canada, Europe, Mexico, and the U.S. The composite of emission inventories corresponds to the public release version of GEOS-Chem v10-01.

We present updated anthropogenic (fossil fuel and biofuel) emissions of  $\text{C}_2\text{H}_6$  for the year 2010 and compare them to a previous  $\text{C}_2\text{H}_6$  emission inventory for the year 2001. We also compare the  $\text{C}_2\text{H}_6$  model simulations based on both emission inventories to a global suite of observations. Our goal is to showcase the differences in anthropogenic emission totals and geographical distributions that are borne out by using different inventories at different points in time. Lastly, we document the impact of  $\text{C}_2\text{H}_6$  on 2010 simulated atmospheric abundances of  $\text{O}_3$  and PAN.

## 2.2. Global Observations

We compare the model simulations to an exhaustive database of recent  $\text{C}_2\text{H}_6$  observations at the surface (2010–2011) and airborne campaigns (2008–2014) (Table 1). All observations are summarized in Table 2, and the regions of interest are depicted in Figure 2. We include surface flask measurements made at the Institute of Arctic and Alpine Research (INSTAAR) Global Monitoring Program from samples collected by the National Oceanic and Atmospheric Administration (NOAA) Global Greenhouse Gas Reference Network (GGGRN) ([http://instaar.colorado.edu/ar1/Global\\_VOC.html](http://instaar.colorado.edu/ar1/Global_VOC.html)),  $\text{C}_2\text{H}_6$  column measurements derived from ground-based Fourier transform infrared (FTIR) solar observations from the Network for the Detection of Atmospheric Composition Change (NDACC, <http://www.ndsc.ncep.noaa.gov/>), and data from recent aircraft campaigns including the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) [*Simpson et al.*, 2011; *Simpson et al.*, 2010], the Hiaper Pole-to-Pole (HIPPO) campaign [*Wofsy et al.*, 2012], the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) [*Blake et al.*, 2014; *Schaffler et al.*, 2014], the 2014 Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) [*Yakovitch and Herndon*, 2014] campaign, and the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) [*Richter et al.*, 2015]. We also include reported surface measurements from the Boulder Atmospheric Observatory (BAO) [*Gilman et al.*, 2013; *Swarthout et al.*, 2013] and data from 43 Chinese cities [*Barletta et al.*, 2005].

**Table 1.** C<sub>2</sub>H<sub>6</sub> Observations From Surface Sites and Airborne Campaigns Used to Evaluate the Model

2010 Surface Flask Measurements From the NOAA/INSTAAR Global VOC Monitoring Program

Figure 2 Region No.	Mission	Location	Period	Reference
1	ARCTAS	40°–180°W, 32°–90°N	Apr and Jun–Jul 2008	<i>Simpson et al.</i> [2010]
2	HIPPO	150°E–84°W, 80°N–67°S	Jan and Oct–Nov 2009, Mar–Apr 2010, Jun–Sep 2011	and <i>Simpson et al.</i> [2011] <i>Wofsy et al.</i> [2012]
3	SEAC4RS	80°–126°W, 19°–50°N	Aug–Sep 2013	<i>Blake et al.</i> [2014]
4	DISCOVER-AQ	103°–105°W, 38°–42°N	Jul–Aug 2014	and <i>Schauffler et al.</i> [2014]
5	FRAPPE	101°–109°W, 38°–42°N	Jul–Aug 2014	<i>Yacovitch and Herndon</i> [2014] <i>Richter et al.</i> [2015]

2010 Column Measurements From the NDACC Network

Code	Site	Location	Altitude (masl)	Reference
<i>North America</i>				
TAO	Toronto, Canada	112°W, 32°N	2158	<i>Wiacek et al.</i> [2007]
BLD	Boulder, Colorado, United States	69°W, 77°N	30	<i>Hannigan et al.</i> [2009]
<i>Europe</i>				
JFJ	Jungfraujoch, Switzerland	8°E, 47°N	3580	<i>Franco et al.</i> [2015]
KRN	Kiruna, Sweden	20°E, 68°N	419	<i>Blumenstock et al.</i> [2009] and <i>Kohlhepp et al.</i> [2011]
<i>North Africa</i>				
IZO	Izaña, Tenerife, Spain	16°W, 28°N	2367	<i>García et al.</i> [2012] and <i>Schneider et al.</i> [2010]

2010 Surface Flask Measurements From the NOAA/INSTAAR Global VOC Monitoring Program

Code	Site	Location	Altitude (masl)
<i>North America</i>			
ALT	Alert, Nunavut, Canada	62.51°W, 82.45°N	205
BMW	Tudor Hill, Bermuda, United Kingdom	64.88°W, 32.26°N	60
BRW	Barrow, Alaska, United States	156.61°W, 71.32°N	16
CBA	Cold Bay, Alaska, United States	162.72°W, 55.21°N	57
KEY	Key Biscayne, Florida, United States	80.16°W, 25.67°N	6
LEF	Park Falls, Wisconsin, United States	90.27°W, 45.95°N	868
MID	Sand Island, Midway, United States	177.38°W, 28.21°N	15
THD	Trinidad Head, California, United States	124.15°W, 41.05°N	112
UTA	Wendover, Utah, United States	113.72°W, 39.9°N	1332
<i>Europe</i>			
HPB	Hohenpeissenberg, Germany	11.02°E, 47.8°N	941
ICE	Storhofdi, Vestmannaeyjar, Iceland	20.29°W, 63.4°N	127
MHD	Mace Head, County Galway, Ireland	9.9°W, 53.33°N	26
OKX	Ochsenkopf, Germany	11.81°E, 50.03°N	1172
PAL	Pallas-Sammaltunturi, GAW Station, Finland	24.12°E, 67.97°N	565
SUM	Summit, Greenland	38.42°W, 72.6°N	3215
ZEP	Ny-Alesund, Svalbard, Norway and Sweden	11.89°E, 78.91°N	479
<i>East Asia</i>			
SHM	Shemya Island, Alaska, United States	174.13°E, 52.71°N	28
TAP	Tae-ahn Peninsula, South Korea	126.13°E, 36.74°N	21
<i>Central America</i>			
KUM	Cape Kumukahi, Hawaii, United States	154.82°W, 19.52°N	8
MEX	High Altitude Global Climate Observation Center, Mexico	97.31°W, 18.98°N	4469
MLO	Mauna Loa, Hawaii, United States	155.58°W, 19.54°N	3402
<i>North Africa</i>			
IZO	Izana, Tenerife, Canary Islands, Spain	16.5°W, 28.31°N	2378
ASK	Assekrem, Algeria	5.63°E, 23.26°N	2715
<i>South Asia</i>			
GMI	Mariana Islands, Guam	144.66°E, 13.39°N	5
<i>Australia</i>			
BKT	Bukit Kototabang, Indonesia	100.32°E, 0.2°S	850
CGO	Cape Grim, Tasmania, Australia	144.69°E, 40.68°S	164



**Table 1.** (continued)

2010 Surface Flask Measurements From the NOAA/INSTAAR Global VOC Monitoring Program

Code	Site	Location	Altitude (masl)	
South Africa				
ASC	Ascension Island, United Kingdom	14.4°W, 7.97°S	90	
CRZ	Crozet Island, France	51.85°E, 46.43°S	202	
HBA	Halley Station, Antarctica, United Kingdom	26.21°W, 75.61°S	35	
MKN	Mt. Kenya, Kenya	37.3°E, 0.06°S	3649	
SEY	Mahe Island, Seychelles	55.53°E, 4.68°S	6	
SYO	Syowa Station, Antarctica, Japan	39.58°E, 69°S	3	
SPO	South Pole, Antarctica, United States	24.8°W, 89.98°S	2815	
South America				
EIC	Easter Island, Chile	109.43°W, 27.16°S	69	
PSA	Palmer Station, Antarctica, United States	64°W, 64.92°S	15	
SMO	Tutuila, American Samoa	170.56°W, 14.25°S	60	
TDF	Tierra Del Fuego, Ushuaia, Argentina	68.31°W, 54.85°S	32	
Surface Observations				
Code/Figure 2 Region No.	Site	Location	Period	Reference
BAO	Boulder Atmospheric Observatory	105.01°W, 40.05°N	Feb–Mar 2011	Gilman et al. [2013]
BAO	Boulder Atmospheric Observatory	105.01°W, 40.05°N	Feb–Mar 2011	Swarthout et al. [2013]
6	43 Chinese cities averaged horizontally every 20° × 10° (longitude, latitude)	100°–130°E, 20°–45°N	Jan–Feb 2001	Barletta et al. [2005]

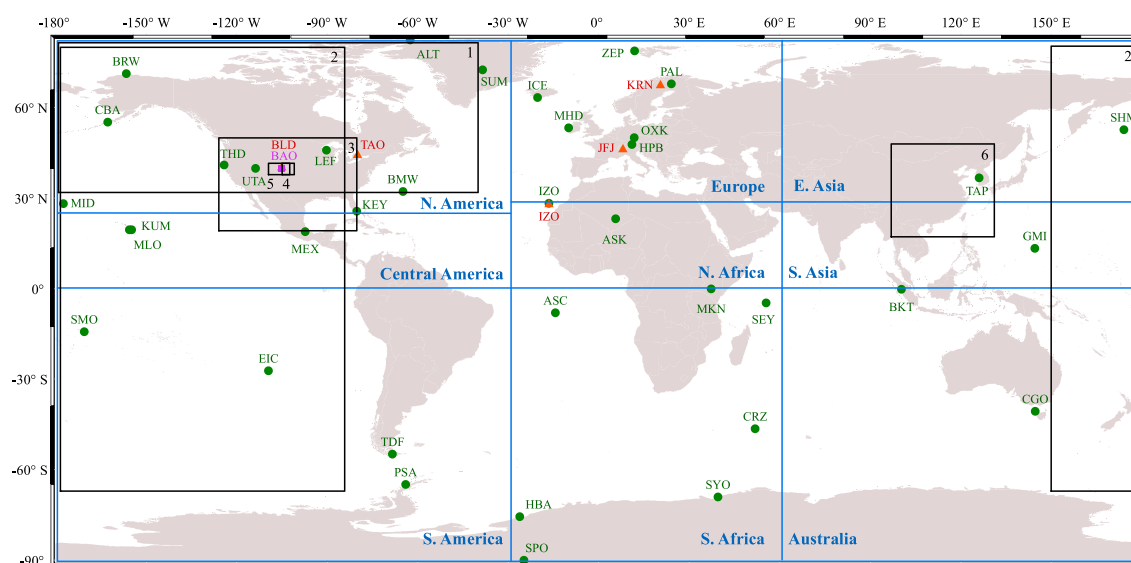
### 2.3. Global C<sub>2</sub>H<sub>6</sub> Emission Inventories

#### 2.3.1. 2001 C<sub>2</sub>H<sub>6</sub> Emission Inventory

Prior to this work, the most recent global C<sub>2</sub>H<sub>6</sub> emission inventory implemented in GEOS-Chem model version 10-01 was based on the year 2001 [Xiao *et al.*, 2008]. The model sets this C<sub>2</sub>H<sub>6</sub> inventory as default for any simulation. Briefly, this inventory is derived from a previous C<sub>2</sub>H<sub>6</sub> emission inventory by Xiao *et al.*

**Table 2.** C<sub>2</sub>H<sub>6</sub> Emissions in Tg yr<sup>−1</sup> by Region for the 2001 and 2010 C<sub>2</sub>H<sub>6</sub> Emission Inventories

Region	Fossil Fuel (Tg yr <sup>−1</sup> )	Biofuel (Tg yr <sup>−1</sup> )	Biomass Burning (Tg yr <sup>−1</sup> )
<i>2001 C<sub>2</sub>H<sub>6</sub> Emission Inventory</i>			
Global	7.9	2.5	2.7
Northern Hemisphere	7.2	2.1	1.1
North America	1.9	<0.05	0.1
Europe	2.1	0.3	<0.05
East Asia	1.6	0.4	0.1
Central America	0.2	0.1	<0.05
North Africa	0.6	0.3	0.4
South Asia	0.8	1.0	0.4
Southern Hemisphere	0.7	0.4	1.7
Australia	0.3	0.1	<0.05
South Africa	0.2	0.2	0.7
South America	0.1	0.2	1.0
<i>2010 C<sub>2</sub>H<sub>6</sub> emission Inventory</i>			
Global	7.1	2.8	2.7
Northern Hemisphere	6.7	2.4	1.1
North America	1.7	<0.05	0.1
Europe	1.6	0.4	<0.05
East Asia	1.9	0.4	0.1
Central America	0.4	0.1	<0.05
North Africa	0.4	0.4	0.4
South Asia	0.8	1.0	0.4
Southern Hemisphere	0.4	0.4	1.7
Australia	0.1	0.1	<0.05
South Africa	0.1	0.3	0.7
South America	0.2	0.1	1.0



**Figure 2.** Regions for  $\text{C}_2\text{H}_6$  emissions analysis and locations of  $\text{C}_2\text{H}_6$  observations. The black boxes cover regions of aircraft measurements, the green circles represent surface flask measurements, the orange triangles locate  $\text{C}_2\text{H}_6$  column measurements, and the purple square shows BAO surface measurements (Table 1). Regions delimited to calculate  $\text{C}_2\text{H}_6$  emissions presented on Table 2 are encompassed by blue boxes.

[2004], which scales  $\text{C}_2\text{H}_6$  emissions to  $\text{CH}_4$  fossil fuel sources by using fixed regional ratios, and bases the geographical distribution for the emissions on data from 1978 to 1986 [Fung et al., 1991; Wang et al., 2004]. Major changes to the distribution of fossil fuel sources may have occurred globally during the period from which they draw data for the model evaluation. Xiao et al. [2008] estimate global  $\text{C}_2\text{H}_6$  emissions for three different source types: (1) fossil fuel, (2) biofuel (domestic wood fuels), and (3) biomass burning. However, the only global  $\text{C}_2\text{H}_6$  emission inventory from Xiao et al. [2008] implemented in GEOS-Chem version 10-01 is from fossil fuel sources. In the model, the  $\text{C}_2\text{H}_6$  emission fluxes from the fossil fuel inventory from Xiao et al. [2008] have no seasonality, and no scaling factors are available to scale them to other years. To simulate global biofuel sources, we use the biofuel  $\text{C}_2\text{H}_6$  emission inventory derived by Yevich and Logan [2003] and the GEFD3 emission inventory [van der Werf et al., 2010] for biomass burning  $\text{C}_2\text{H}_6$  emissions.

### 2.3.2. 2010 $\text{C}_2\text{H}_6$ Emission Inventory

#### 2.3.2.1. Global $\text{C}_2\text{H}_6$ Emissions

We develop an updated global  $\text{C}_2\text{H}_6$  emission inventory for 2010, by scaling  $\text{C}_2\text{H}_6$  to  $\text{CH}_4$  emissions following a similar approach to previous studies [Blake and Rowland, 1986; Etiope and Ciccioli, 2009; Franco et al., 2016; Rudolph, 1995; Xiao et al., 2004; Xiao et al., 2008]. There are many approaches that can be used to estimate  $\text{CH}_4$  emissions (i.e., top-down studies, bottom-up models, inventories, and data-driven approaches), and differing approaches can yield different emission totals, attribution, or geographical distributions [Saunio et al., 2016]. In this study, the  $\text{CH}_4$  fluxes were derived from the Greenhouse Gases Observing SATellite (GOSAT) by Turner et al. [2015] for the year 2010. To derive anthropogenic  $\text{CH}_4$  emissions, Turner et al. [2015] used a priori emissions from EDGAR v4.2 (<http://edgar.jrc.ec.europa.eu/>). The EDGAR emission inventory combines Tier 1 and region-specific Tier 2 emission factors, which have multiple uncertainties associated with them. A detailed description of these uncertainties is presented by Olivier [2002]. The estimated uncertainty of satellite  $\text{CH}_4$  single retrievals is 0.8% [Parker et al., 2011]. A description of the error characterization and the uncertainties associated with the North American  $\text{CH}_4$  inversions can be found in Turner and Jacob [2015]. Turner et al. [2015] infer a 2009–2011 U.S. anthropogenic emission source of  $40.2\text{--}42.7\text{ Tg a}^{-1}$  and attribute 22–31% to oil and gas activities. Other inverse studies have inferred a larger range of anthropogenic emissions ( $30.0\text{--}44.5\text{ Tg a}^{-1}$ ) [see Turner et al., 2015, and references within]. It is important to note that, over regions with  $\text{CH}_4$  emissions from oil and natural gas activities and livestock, the source attribution is very sensitive to assumptions made in the prior distribution. Uncertainties associated with the  $\text{CH}_4$  emissions, or their attribution, are only one of several sources of uncertainty in using  $\text{CH}_4$  fluxes to estimate  $\text{C}_2\text{H}_6$  fluxes. As we discuss later in this section, a second major issue is the choice of  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratio.

We implement two grid resolutions for the *Turner et al.* [2015] CH<sub>4</sub> fluxes for the year 2010. For North America, we use CH<sub>4</sub> emission fluxes at  $1/2^\circ \times 2/3^\circ$  resolution and at  $4^\circ \times 5^\circ$  resolution for the rest of the world. Considering the uncertainties in the attribution of fluxes, we expect a better agreement of CH<sub>4</sub> anthropogenic sources at a coarse resolution compared to the finer resolution. We can have the most confidence in the total fluxes, rather than fine sectorial attribution. From the 12 anthropogenic CH<sub>4</sub> source categories derived in *Turner et al.* [2015], 3 are relevant to C<sub>2</sub>H<sub>6</sub>: natural gas activity, biofuel usage, and biomass burning.

We consider natural gas activity and biofuel source categories and retain the GFED3 emission inventory for emissions of C<sub>2</sub>H<sub>6</sub> from biomass burning during 2010. We treated biofuel consumption (both from home cooking and heating) as residential biomass burning and thus applied a temperate forest fuel ratio of 15.2 (% mol C<sub>2</sub>H<sub>6</sub>/mol CH<sub>4</sub>), as estimated by *Akagi et al.* [2011]. To derive C<sub>2</sub>H<sub>6</sub> emissions from CH<sub>4</sub> fluxes associated with natural gas activity, we used a ratio of 4.3 (% mol C<sub>2</sub>H<sub>6</sub>/mol CH<sub>4</sub>) based on mixing ratio enhancements estimated from the South Central U.S. by *Katzenstein et al.* [2003]. *Warneke et al.* [2014] observed similar emission ratios during wintertime 2012 over the Uintah Basin. In this study, we assume that the observed enhancement ratios (slopes of the linear fits) are approximately equivalent to the emission ratios since C<sub>2</sub>H<sub>6</sub> is a relatively long-lived species and in situ measurements are taken close to the sources.

#### 2.3.2.2. Constraints on C<sub>2</sub>H<sub>6</sub> Emissions Over Mexico and Asia

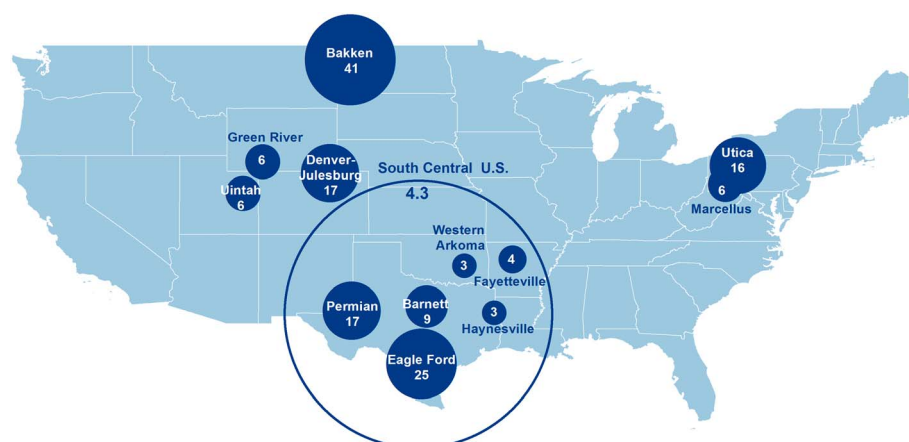
An analysis of the resulting global C<sub>2</sub>H<sub>6</sub> emissions immediately points to likely problems with the underlying CH<sub>4</sub> fluxes or the 4.3 (% mol C<sub>2</sub>H<sub>6</sub>/mol CH<sub>4</sub>) ratio over Mexico and Asia. Also, estimated fossil fuel C<sub>2</sub>H<sub>6</sub> emission totals derived from CH<sub>4</sub> fluxes over Mexico are 2 times higher (0.23 Tg) than the 2001 C<sub>2</sub>H<sub>6</sub> emission inventory. Similar differences of 0.36 Tg and 0.13 Tg occur when comparing to RETRO (REanalysis of the TROpospheric chemical composition 2000, [http://gcmd.gsfc.nasa.gov/records/GCMD\\_GEIA\\_RETRO.html](http://gcmd.gsfc.nasa.gov/records/GCMD_GEIA_RETRO.html)) and Global Emissions Initiative 1985 (<http://www.geiacenter.org>) emission inventories, respectively. Additionally, when analyzing the spatial distribution of fossil fuel C<sub>2</sub>H<sub>6</sub> emissions over Mexico derived from CH<sub>4</sub> fluxes, we find that the C<sub>2</sub>H<sub>6</sub> emission sources are located away from oil and natural gas production areas. Second, total fossil fuel satellite-derived emissions of C<sub>2</sub>H<sub>6</sub> over Asia are half (~1.2 Tg) of the 2001 C<sub>2</sub>H<sub>6</sub> emission inventory and RETRO, respectively. A simulation with these emissions produces C<sub>2</sub>H<sub>6</sub> mixing ratios that are 1/6 of the observed mixing ratios during wintertime in 2001 by *Barletta et al.* [2005] (note also the time difference between these in situ observations (2001) and the inversion (2010)). Finally, a comparison between the spatial distribution of fossil fuel C<sub>2</sub>H<sub>6</sub> emissions over China from the 2010 C<sub>2</sub>H<sub>6</sub> emission inventory and the emissions derived from CH<sub>4</sub> fluxes shows that the C<sub>2</sub>H<sub>6</sub> emissions from CH<sub>4</sub> fluxes are clustered in south central China, while the *Xiao et al.* [2008] C<sub>2</sub>H<sub>6</sub> emission distribution covers urban and known oil and natural gas-producing regions in China. In summary, there is evidence that scaling C<sub>2</sub>H<sub>6</sub> emissions derived from CH<sub>4</sub> fluxes does not produce realistic C<sub>2</sub>H<sub>6</sub> emission over Mexico and China. In order to address the two regional discrepancies above, we substitute the C<sub>2</sub>H<sub>6</sub> emissions derived from CH<sub>4</sub> fluxes with the *Xiao et al.* [2008] C<sub>2</sub>H<sub>6</sub> emission inventory over Mexico and Asia (including China, India, Indonesia, Japan, Mongolia, and North and South Korea).

#### 2.3.2.3. Constraints on C<sub>2</sub>H<sub>6</sub> Emissions Over the U.S.

The NEI 2011 emission data are provided by state and local agencies based on industrial, commercial, and area sources. We incorporate NEI 2011 version 2 C<sub>2</sub>H<sub>6</sub> emissions on a  $0.1^\circ \times 0.1^\circ$  grid for biofuel and six anthropogenic source categories, including oil and gas activities [*U.S. Environmental Protection Agency*, 2013]. GEOS-Chem version 10-01 uses a scaling factor of 1.016 to apply NEI 2011 C<sub>2</sub>H<sub>6</sub> emissions to the year 2010. For other species such as CO, NO, and other VOCs, scaling factors are assigned based on government statistics and documents. For industrial emissions, the scaling factors are based on reported trends from the Environmental Protection Agency Acid Rain Program (<https://www.epa.gov/airmarkets/acid-rain-program>). For other emissions the scaling factors come from the National Emissions Inventory Air Pollutant Emissions Trends data (<https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>).

The NEI 2011 C<sub>2</sub>H<sub>6</sub> emission sources appear to align with the distribution of active oil and natural wells over the U.S. (see Figure 5); however, when the GEOS-Chem-simulated C<sub>2</sub>H<sub>6</sub> is compared to aircraft measurements over the U.S. from five recent field campaigns (2008–2014) and 2010 surface flask observations from the NOAA GGRN, the use of the NEI 2011 emissions produces mixing ratios at the surface and throughout the column that are 14–50% of those observed. Consequently, we tested uniformly scaling C<sub>2</sub>H<sub>6</sub> emissions from all the categories in the NEI 2011 by factors between 1.2 and 2, and we compared the results to the



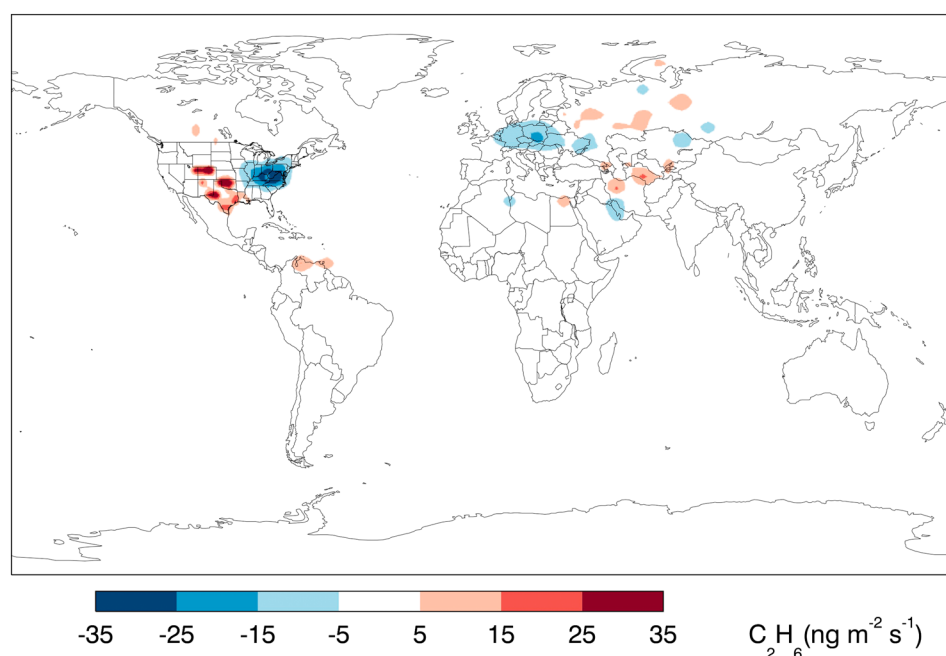


**Figure 3.** Spatial distribution of averaged percentage molar  $\text{C}_2\text{H}_6/\text{CH}_4$  ratios in oil and natural gas basins over the contiguous U.S. The values and sizes of the circles represent the magnitude of the ratios in each basin. South Central U.S.: calculated using annual emissions of  $\text{C}_2\text{H}_6$  and  $\text{CH}_4$  reported by Katzenstein *et al.* [2003]. Bakken: Brandt *et al.* [2015] as reported by Kort *et al.* [2016]. Barnett: Speight [2013] as reported by Kort *et al.* [2016]. Denver-Julesburg: Peischl *et al.* [2015a]. Eagle Ford: Conder and Lawlor [2014] and Ghandi *et al.* [2015] as reported by Kort *et al.* [2016]. Fayetteville: average from Peischl *et al.* [2015b] and Speight [2013] as reported by Kort *et al.* [2016]. Green River: Peischl *et al.* [2015a]. Haynesville: average from Peischl *et al.* [2015b] and Speight [2013] as reported by Kort *et al.* [2016]. Marcellus: average from Peischl *et al.* [2015b], 2009 U.S. Geological Survey (USGS) database as reported by Peischl *et al.* [2015b], and Conder and Lawlor [2014] as reported by Kort *et al.* [2016]. Permian: Peischl *et al.* [2015a]. Western Arkoma: average from Peischl *et al.* [2015b], 2009 U.S. Geological Survey (USGS) database as reported by Peischl *et al.* [2015b]. Uintah: average from Helmig *et al.* [2014b] and Warneke *et al.* [2014]. Utica: Conder and Lawlor [2014] and Ghandi *et al.* [2015] as reported by Kort *et al.* [2016].

observations. For all factors, a linear regression of 2010 monthly mean surface flask observations over the U.S. versus model output yields coefficient of determination ( $R^2$ ) values between 0.59 and 0.64. The slopes range from 0.8 to 1.0. Of the scaling factors tested, 1.4 produces the best agreement between the GEOS-Chem simulation and observations in regions *without* major oil and gas operations. Therefore, we multiplied NEI 2011  $\text{C}_2\text{H}_6$  emissions by 1.4, which represents an addition of 0.5 Tg of  $\text{C}_2\text{H}_6$  compared to the base NEI 2011. Scaling beyond 1.4 results in an overestimate of observations in these regions. Following the adjustment of NEI 2011  $\text{C}_2\text{H}_6$  emissions, we refer to the resulting global  $\text{C}_2\text{H}_6$  emission inventory as 2010  $\text{C}_2\text{H}_6$  emission inventory. Thus, the 2010  $\text{C}_2\text{H}_6$  emission inventory combines a global  $\text{C}_2\text{H}_6$  emission inventory derived from satellite  $\text{CH}_4$  observations, except for Mexico and Asia where we apply previous emission estimates, and a regional  $\text{C}_2\text{H}_6$  emission inventory derived by adjusting NEI 2011  $\text{C}_2\text{H}_6$  emissions.

#### 2.3.2.4. Uncertainties

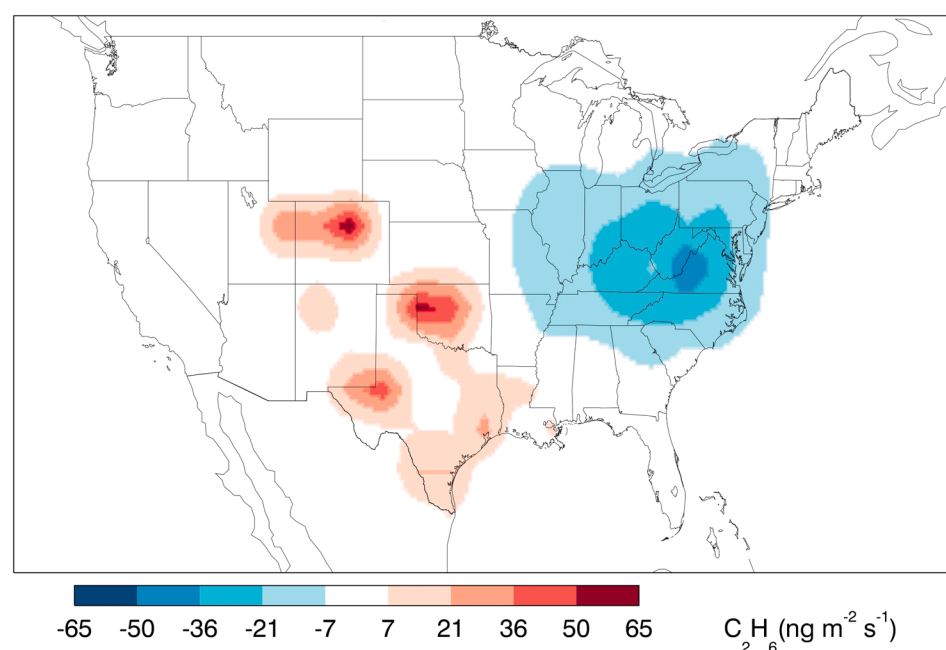
Although the approach of deriving  $\text{C}_2\text{H}_6$  from  $\text{CH}_4$  emissions is consistent with past global budget studies, large uncertainties are associated with the use of few  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratios, especially for the natural gas industry, which in the last decade has been subject to multiple emission controls in many countries. Emission ratios depend on the type of oil and natural gas reservoir (e.g., tight gas versus shale gas), the VOC composition of the natural gas [Warneke *et al.*, 2014], the production stage of a producing well [Kang *et al.*, 2014; Pacsi *et al.*, 2015], among other characteristics. There has been significant attention devoted to documenting  $\text{C}_2\text{H}_6$  to  $\text{CH}_4$  enhancement ratios. Given the lifetime of each species, enhancement ratios observed near defined sources are often a reasonable surrogate for emission ratios. Figure 3 presents a summary of averaged percentage molar  $\text{C}_2\text{H}_6/\text{CH}_4$  ratios observed in different oil and natural gas basins over the contiguous U.S. The reported ratios (% mol  $\text{C}_2\text{H}_6/\text{mol CH}_4$ ) have a large range; for example, Kort *et al.* [2016] report 40.5 for the Bakken, more than an order of magnitude larger than the ratio reported for some oil and gas basins in the central U.S. [Peischl *et al.*, 2015b]. There are a number of problems associated with basing  $\text{C}_2\text{H}_6$  emissions on  $\text{CH}_4$  emissions and dynamic  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratios. As we will show later, using a constant  $\text{C}_2\text{H}_6/\text{CH}_4$  emission ratio over regions with high emission gradients (e.g., U.S.) does not represent the geographical distributions of the emissions and the resulting atmospheric abundances of  $\text{C}_2\text{H}_6$ . Section 4.1 presents the sensitivity of our findings to the choice of  $\text{C}_2\text{H}_6$ -to- $\text{CH}_4$  molar ratios through simulations with a fixed ratio applied broadly across the U.S. by using the low and high ratios available from the recently published literature (Figure 3).



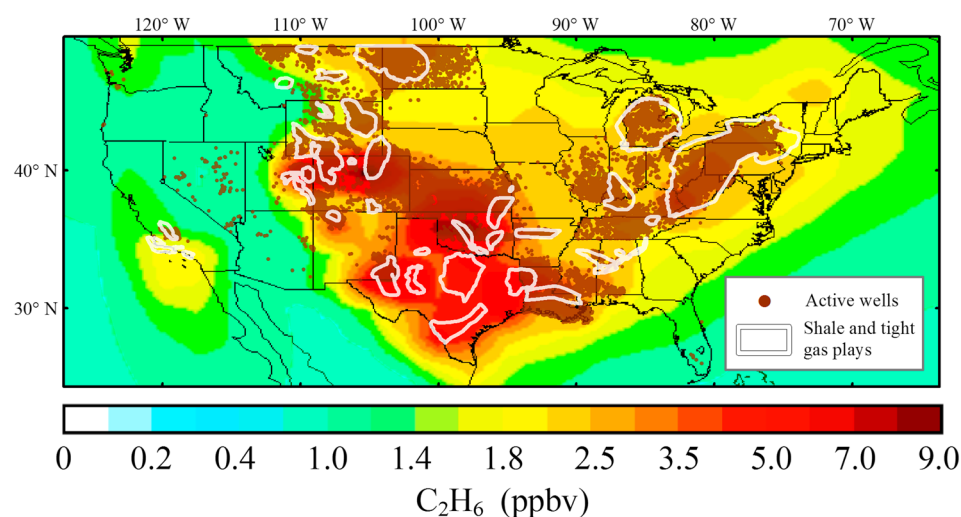
**Figure 4.** Global comparison between modeled distributions of fossil fuel  $C_2H_6$  emissions for 2001 and 2010  $C_2H_6$  emission inventories (2010–2001). The positive values (warmer colors) represent increases in modeled annual mean  $C_2H_6$  emission fluxes.

### 2.3.3. Comparison Between the 2001 and 2010 $C_2H_6$ Emission Inventories

Table 2 shows global and regional  $C_2H_6$  emission estimates for both emission inventories. For the 2010  $C_2H_6$  emission inventory, Northern Hemisphere fossil fuel sources represent half of global  $C_2H_6$  emissions and 95% of global fossil fuel emissions.



**Figure 5.** Comparison between modeled distributions of fossil fuel  $C_2H_6$  emissions for 2001 and 2010  $C_2H_6$  emission inventories (2010–2001) over the U.S. The positive values (warmer colors) represent increases in modeled annual mean  $C_2H_6$  emission fluxes.



**Figure 6.** Modeled annual mean surface mixing ratios of the 2010  $C_2H_6$  emission inventory and spatial distribution of active wells (FracTracker, accessed Nov 2015, [www.fractracker.org](http://www.fractracker.org); data for Maryland, North Carolina, and Texas are missing). Shale and tight gas plays (Energy Information Administration, accessed Dec 2014, [www.eia.gov/dnav/ng/ng\\_sum\\_lsum\\_a\\_EPGO\\_xdg\\_count\\_a.htm](http://www.eia.gov/dnav/ng/ng_sum_lsum_a_EPGO_xdg_count_a.htm)) are shown to provide a sense for well distribution over states where well location data are missing.

The  $C_2H_6$  emission totals are only subtly different between both global inventories; however, the spatial distributions of the emissions are quite distinct. In our recommended 2010 inventory,  $C_2H_6$  emissions increase over intense oil and gas-producing regions, including the central and northeastern U.S., Venezuela, eastern Russia, and the northern part of the Middle East (Figure 4). We point this out because it may indicate that emissions from the oil and natural gas industry in these regions could be important but may not be accounted for in commonly used inventories. Over Europe, Xiao *et al.* [2008] concluded that their inventory overestimated the observed  $C_2H_6$  mixing ratios by 20–30%, and they attributed this in part to an overestimation of European sources. Our 2010  $C_2H_6$  emission inventory shows a similar reduction of  $C_2H_6$  European sources (Table 2). Over the contiguous U.S., we find important differences in the geographical distribution and magnitude when comparing the fossil fuel  $C_2H_6$  emission fluxes from the 2010  $C_2H_6$  emission inventory to the Xiao *et al.* [2008] 2001 emission inventory (Figure 5). Fossil fuel  $C_2H_6$  emission fluxes are smaller over the northeastern part and larger over the central and south central parts of the U.S.

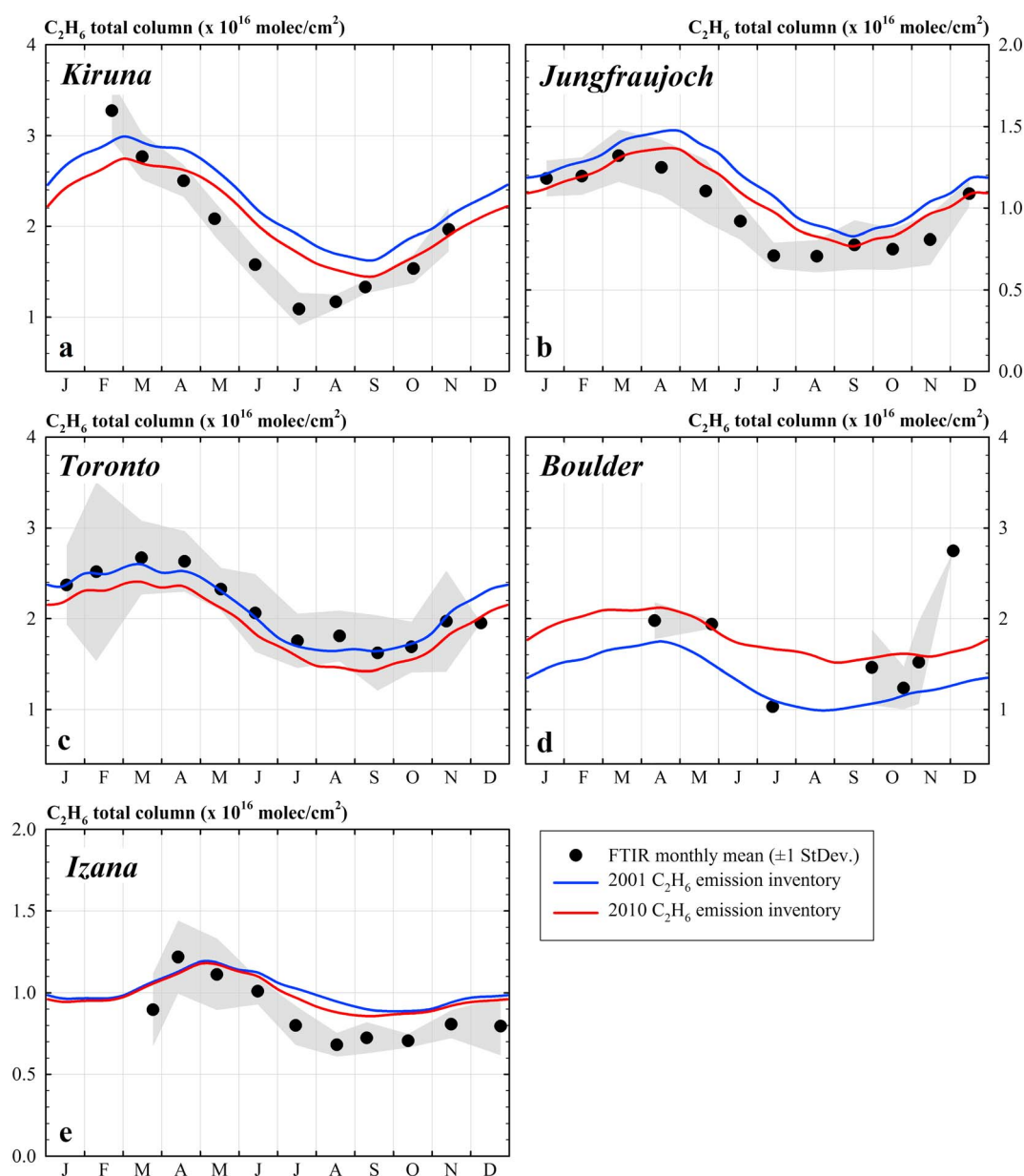
The 2010  $C_2H_6$  emission inventory shows increased emission regions encompassing major U.S. natural gas production basins (Figure 6). The simulated surface  $C_2H_6$  abundances produced by the 2010  $C_2H_6$  emission inventory closely align with oil and gas activities over the U.S. Although the 2010  $C_2H_6$  emissions show significant increases in fossil fuel  $C_2H_6$  emissions over these regions, they continue to underestimate the most recent vertical and surface observations of  $C_2H_6$  mixing ratios over the central U.S., as described in section 4. Despite the underestimation of  $C_2H_6$  abundances over the central U.S., the 2010  $C_2H_6$  emission inventory produces a better geographical distribution of fossil fuel  $C_2H_6$  sources over North American regions and elsewhere compared to the 2001  $C_2H_6$  emission inventory.

### 3. Model Evaluation

#### 3.1. Ground-Based $C_2H_6$ Column Observations

Comparisons between each modeled emission inventory and monthly mean  $C_2H_6$  total columns at selected NDACC stations over the Northern Hemisphere for both  $C_2H_6$  emission inventories are shown in Figure 7. We note that observations over Northern Hemisphere continental regions such as Asia and the Middle East are needed to evaluate model outputs in other oil and natural gas-producing regions.

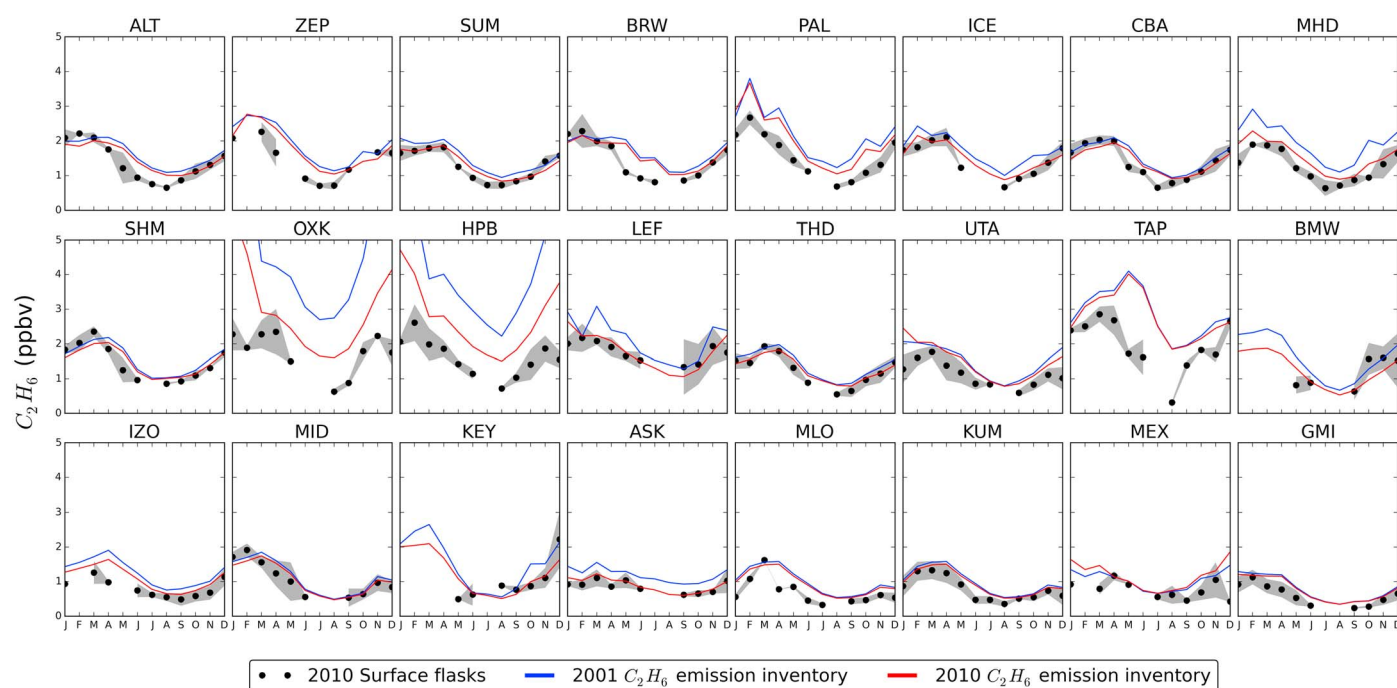
Ethane columns are derived from ground-based FTIR solar observations following the methodology presented by Franco *et al.* [2015]. The information content as well as the vertical sensitivity for the FTIR retrievals from all the sites we analyze in this paper is similar to the one presented in Franco *et al.* [2015]. At



**Figure 7.** Comparison of 2010  $\text{C}_2\text{H}_6$  total columns to modeled 2001 and 2010  $\text{C}_2\text{H}_6$  emission inventories. The black dots represent monthly mean  $\text{C}_2\text{H}_6$  total columns, and the grey areas denote their associated  $1\sigma$  standard deviation. The lines represent modeled total columns for different emission inventories.

altitudes below 13 km, 99% of the information content is independent from the a priori profile, indicating a very good sensitivity to the true state of the atmosphere [Franco et al., 2015].

The FTIR total column observations largely reflect the tropospheric background, and not solely the surface  $\text{C}_2\text{H}_6$  abundances. Thus, similarities between our two simulations can be expected, particularly since most FTIR stations involved here are not located in source regions and  $\text{C}_2\text{H}_6$  has a relative long lifetime that allows emissions to impact abundances at a hemispheric scale. Our model simulations largely reproduce  $\text{C}_2\text{H}_6$  column observations at the selected stations, suggesting that the OH losses and emissions of other OH-reactive species are being well represented. Additionally, the spatial variability indicates that the model reproduces the major features of  $\text{C}_2\text{H}_6$  emissions and the most important transport processes. The agreement with observations is particularly good at Toronto and Boulder (see Figure 10; explained on section 4.2). However, during summertime, GEOS-Chem overestimates the  $\text{C}_2\text{H}_6$  column at three sites (Izana, Kiruna, and Jungfraujoch;



**Figure 8.** Comparison of Northern Hemisphere 2010  $C_2H_6$  surface mixing ratios to modeled 2001 and 2010  $C_2H_6$  emission inventories. The black dots represent  $C_2H_6$  observations from NOAA GGGRN global surface flask network, and the grey areas denote their associated  $1\sigma$  standard deviation. The lines represent model mixing ratios at the surface from both  $C_2H_6$  emission inventories. The stations are ordered from higher to lower latitudes.

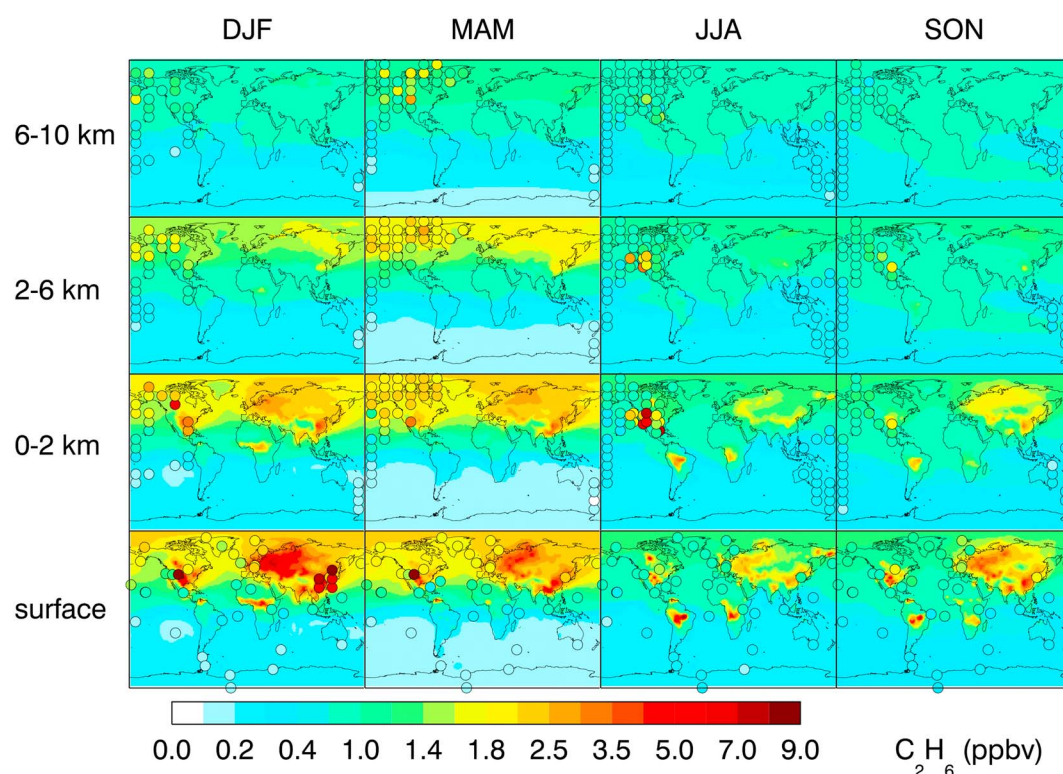
Figures 7a, 7b, and 7e). A similar bias was also reported by *Franco et al.* [2016] over remote sites in the Arctic and the Tropics. The same version of the GEOS-Chem model we use here was also used in that study, and the summertime bias may be driven by  $\sim 10$ – $15\%$  lower global mean OH in GEOS-Chem version 10-01 compared to previous versions. *Xiao et al.* [2008] used GEOS-Chem version 6.01.03, and their results do not show a summertime bias compared to surface data. GEOS-Chem version 6.01.03 had a 15% greater  $C_2H_6$ -OH rate constant ( $8.7 \times 10^{-12} \exp(-1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [Sander et al., 2003]) and  $\sim 3\%$  lower annual mean OH concentration ( $10.2 \times 10^5 \text{ molecules cm}^{-3}$ ) compared to GEOS-Chem version 10-01 used in this study.

### 3.2. Surface Observations

Figure 8 presents a comparison between 2010 Northern Hemisphere  $C_2H_6$  surface mixing ratios and the 2001 and 2010  $C_2H_6$  emission inventories. The Southern Hemisphere comparison is presented in Figure S1 in the supporting information. In both figures, sampling stations are ordered from higher to lower latitudes. The NOAA sampling stations are mostly located at remote locations around the globe, largely avoiding the impact of local anthropogenic emissions.

Mixing ratios at the surface reflect the  $C_2H_6$  latitudinal gradient with values decreasing with decreasing latitude. Our model simulations largely capture the  $C_2H_6$  seasonal cycles. However, the model overestimates surface mixing ratios over Europe (Ochsenkopf (OXK) and Hohenpeissenberg (HPB) stations) by  $\sim 160\%$  and  $\sim 80\%$  on average for the 2001 and 2010  $C_2H_6$  emission inventories, respectively. The difference between the model outputs and the observations might be due to an overestimation of European sources. The overestimation we find when simulating 2010  $C_2H_6$  emissions may be related to incorrect source attribution of European  $C_2H_6$  anthropogenic sources derived from the EDGAR v4.2 inventory used as a prior for the satellite-derived  $CH_4$  fluxes. In Asia, the model overpredicts the  $C_2H_6$  abundance at the Tae-ahn Peninsula (TAP) station located in the southern part of South Korea by  $\sim 1$  ppbv throughout the year. TAP is likely heavily influenced by emissions from both Russia and China. However, a comparison with surface measurements in 43 Chinese cities [Barletta et al., 2005] shows that the model underpredicts surface mixing ratios for the 2001 wintertime by up to a factor of 3. Given the limited and outdated observations in this region, we cannot determine whether this is a result of





**Figure 9.** Global mean distribution of  $C_2H_6$  for different seasons and altitude ranges compared to observations from Table 1. The background solid contours are model outputs for 2010  $C_2H_6$  emissions. The filled circles represent seasonal averages from observations. Aircraft measurements (0–2, 2–6, and 6–10 km) are averaged vertically for each altitude range and horizontally every  $20^\circ \times 10^\circ$  (longitude, latitude). Wintertime surface measurements over 43 Chinese cities are averaged horizontally every  $20^\circ \times 10^\circ$  (longitude, latitude). The overlapping circles represent averaged results from various observations.

incorrect emissions or an incorrect distribution of emissions. Compared to the rest of the observations we show, there is also a large temporal mismatch between the simulation year (2010) and the Chinese observations (2001). Although our analysis focuses on the Northern Hemisphere, we note that, over the Southern Hemisphere, the station Cape Grim (CGO), located in Tasmania, Australia, is the only station (Figure S1) with large differences between simulations and observations. Specifically, 2001  $C_2H_6$  emissions produce mixing ratios at the surface almost twice as large as those observed. This difference can be attributed to lower  $C_2H_6$  emissions derived from  $CH_4$  satellite observations compared to the 2001  $C_2H_6$  emission inventory.

### 3.3. Vertical Distribution

A comparison between the observed global distribution of  $C_2H_6$  and the GEOS-Chem model output for 2010  $C_2H_6$  emissions from the surface to 10 km is presented in Figure 9. The background solid contours are the model output from 2010, and the filled circles represent the seasonal averages from the observations compiled in Table 2. Measurements at the surface (lower panel) correspond to seasonal averages from the 2010 surface flask-sampling sites and two measurements taken at the Boulder Atmospheric Observatory (BAO) in Colorado, U.S., during February and March of 2011 [Gilman *et al.*, 2013; Swarthout *et al.*, 2013]. The aircraft observations are plotted as the averages for each altitude range for individual  $20^\circ \times 10^\circ$  grid boxes. We plot the data this way, instead of averaged vertical profiles for individual regions/campaigns, because the observations show large gradients over relatively small areas. We compare the model output from 2010 to the aircraft observations collected over the period of 2008–2014. Since the aircraft data represent a relatively short snapshot of time (15–59 flights over 3–20 weeks), this represents a source of uncertainty in the model evaluation as the model output represents seasonal averages.

Surface measurements are generally well simulated by the model throughout the year. However, during the winter, the model tends to overpredict the surface mixing ratios over Europe. The vertical distribution of

C<sub>2</sub>H<sub>6</sub> mixing ratios over the U.S. will be discussed in the next section. A comparison between Northern Hemisphere observations and modeled mixing ratios outside the U.S. (not shown) reveals that springtime C<sub>2</sub>H<sub>6</sub> mixing ratios from HIPPO over latitudes  $< \sim 35^\circ$  are the most underpredicted observations (up to 1.5 ppbv). Springtime HIPPO measurements were taken during the same year of the model simulation and the 2010 C<sub>2</sub>H<sub>6</sub> emission inventory. The missing C<sub>2</sub>H<sub>6</sub> source might be due to an underestimation of biomass burning over the tropics and subtropics or potentially point to remaining issues with East Asian emission inventories.

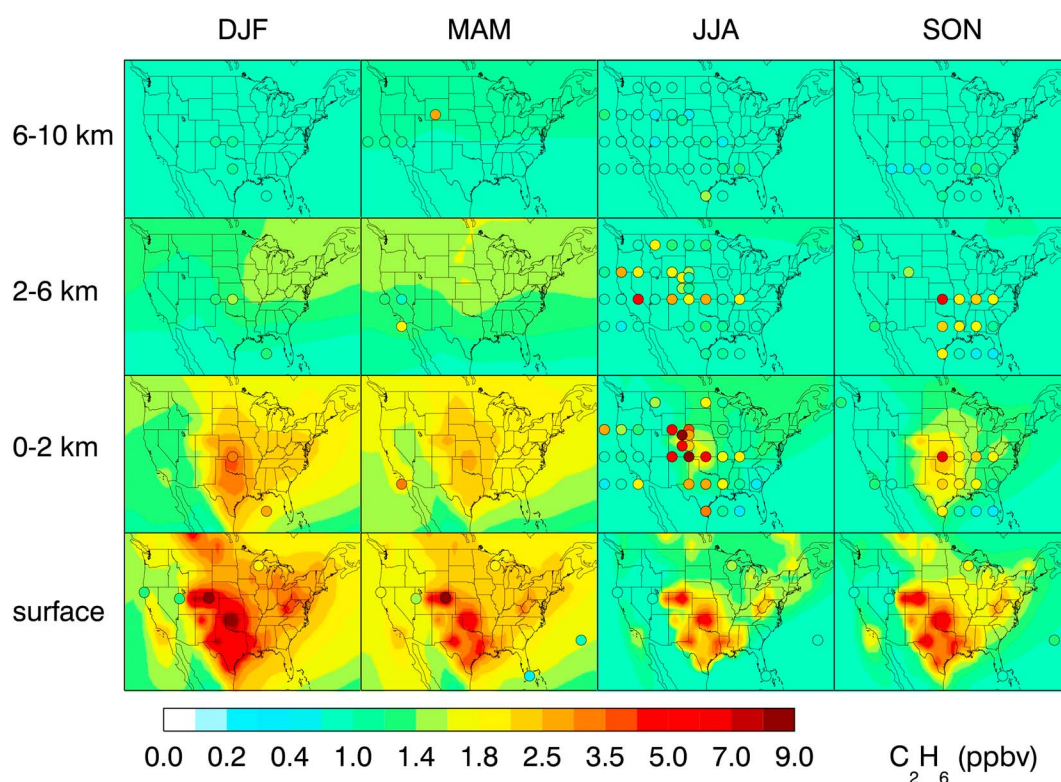
## 4. Model-Data Comparison Over the Contiguous U.S.

### 4.1. Model Comparison to Aircraft Campaigns and Surface Observations

Multiple recent field campaigns, as well as surface observations over the contiguous U.S., allow us to deepen our analysis of anthropogenic C<sub>2</sub>H<sub>6</sub> sources and their regional effects on atmospheric mixing ratios. Figure 10 presents a comparison between the observed distribution of C<sub>2</sub>H<sub>6</sub> and the GEOS-Chem model output for 2010 C<sub>2</sub>H<sub>6</sub> emissions over the U.S. At the surface (lower panel), we show seasonal averages from five surface flask-sampling stations and two sets of measurements collected at the Boulder Atmospheric Observatory during February and March of 2011 [Gilman *et al.*, 2013; Swarthout *et al.*, 2013]. In this figure, aircraft measurements (0–10 km above the ground) were averaged vertically for each altitude range and horizontally every  $5^\circ \times 5^\circ$ .

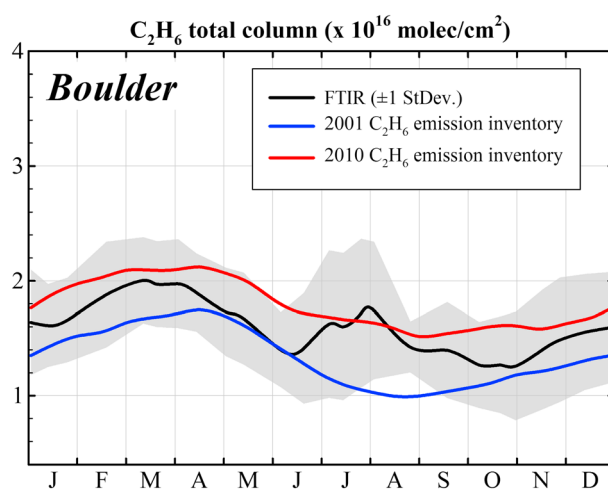
In the upper troposphere (upper panel; 6–10 km) the model agrees with the observations except for the central U.S. Here the model overestimates the summertime observed mixing ratios by up to a factor of  $\sim 3$  (0.5 ppbv). Below 6 km, the model is consistently lower than the observations over the central and southeast U.S. Despite scaling up the NEI 2011 emissions, the model continues to underpredict by a factor of  $\sim 4$  the observed abundances of C<sub>2</sub>H<sub>6</sub> in the central states of Colorado, Wyoming, Nebraska, and Kansas where there is substantial natural gas and oil extraction (Figure 6). The model resolution of  $2^\circ \times 2.5^\circ$  can explain some of the discrepancies between the observations and the model output. Also, we note that the data presented in Figure 10 are primarily from aircraft campaigns and the uncertainties (as discussed in section 2.3.2) associated to the temporal mismatch between the aircraft data (2008–2014) and the model (2010) can potentially be greater due to the increase of oil and natural gas extraction over the U.S. during this period [U.S. Environmental Protection Agency, 2015]. There are greater discrepancies between the most recent field campaigns (SEAC4RS [Blake *et al.*, 2014; Schauffler *et al.*, 2014], DISCOVER-AQ [Yacovitch and Herndon, 2014], and FRAPPÉ [Richter *et al.*, 2015]) and the 2010 model outputs. In order to explore this issue, we used the observed  $5\% \text{ yr}^{-1}$  annual rate of change of C<sub>2</sub>H<sub>6</sub> total column over the 2009–2014 time period at midlatitudes reported by Franco *et al.* [2016] to scale the observations to the year 2010. Unfortunately, underpredictions of mixing ratios across the entire column persist, suggesting that the annual rates of change over these intense oil and natural gas regions are greater than  $5\% \text{ yr}^{-1}$  (as reported at the Boulder FTIR station [Franco *et al.*, 2016]). We cannot rule out the influence of smoke plumes on aircraft measurements during SEAC4RS, since 6 out of 26 flights intercepted smoke plumes. However, the FRAPPÉ flights did not intercept major biomass burning plumes, suggesting that neither agricultural burning nor wildfire smoke is responsible for the observed discrepancy, at least during summer 2014. The wide spatial coverage of the underprediction suggests a regional impact of oil and natural gas emissions to C<sub>2</sub>H<sub>6</sub> mixing ratios.

To investigate the impact of considering the most extreme measured molar C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> ratio observed over oil and natural gas regions, we did an additional simulation to derive global C<sub>2</sub>H<sub>6</sub> emissions from CH<sub>4</sub> fluxes of fossil fuels, but using a value of 40.5 (percentage of mol C<sub>2</sub>H<sub>6</sub>/mol CH<sub>4</sub>) [Kort *et al.*, 2016]. This extreme choice results in C<sub>2</sub>H<sub>6</sub> emissions that are  $\sim 7$  times greater than the NEI 2011 oil and gas source category. Even though the higher molar ratio (40.5 percentage of mol C<sub>2</sub>H<sub>6</sub>/mol CH<sub>4</sub>) is based on observations taken over the Bakken basin, the use of this ratio produces atmospheric C<sub>2</sub>H<sub>6</sub> distributions consistent with aircraft observations over the U.S. central region up to 6 km above the ground. The similar values are consistent with the strong underestimation of the underlying NEI 2011 C<sub>2</sub>H<sub>6</sub> emissions over the Central U.S. It is not appropriate to apply the Bakken molar ratio broadly, but the improvement in representing observed mixing ratios over intense oil and natural gas regions suggests that where sufficient information is available, the use of regional emission ratios instead of a fixed nationwide value for all anthropogenic sources may better reproduce C<sub>2</sub>H<sub>6</sub> atmospheric abundances. Emission impacts from basins/regions with rapid increase oil and natural gas



**Figure 10.** Mean mixing ratios of 2010  $C_2H_6$  emissions over the U.S. for different seasons and altitude ranges compared to observations from Table 1. The background solid contours are model outputs. The filled circles represent seasonal averages from observations. Aircraft measurements (0–2, 2–6, and 6–10 km) were averaged vertically for each range of altitude and horizontally every  $5^\circ \times 5^\circ$  (longitude, latitude). The overlapping circles represent averaged results from various observations.

production like the Bakken shale [Kort *et al.*, 2016] could be better represented by using local emission estimates, which account for the type of oil and natural gas reservoir and the local VOC composition of the natural gas. Our simulations do not show significant emissions from the Bakken shale since the rapid production increase of this basin began in the year 2010 (same year of our simulation [Peischl *et al.*, 2016]).



**Figure 11.** Comparison of  $C_2H_6$  total column to 2010 model output at the Boulder site. The black line represents measurements of  $C_2H_6$  total columns over the period of 2010–2014 detrended and scaled to the year 2010 and the grey areas their associated  $1\sigma$  standard deviation. The blue and red lines represent modeled total columns for different emission scenarios. We note that 2012 was a high wildfire year for the Rocky Mountain region.

## 4.2. Boulder $C_2H_6$ Column Observations

Over the U.S., we present the results of the 2010  $C_2H_6$  column measurements from the National Center for Atmospheric Research Boulder station in Figure 7. The Boulder station is located in a region with intensive oil and natural gas production [Gilman *et al.*, 2013; Pétron *et al.*, 2012; Pétron *et al.*, 2014; Swarthout *et al.*, 2013; Thompson *et al.*, 2014]. Unfortunately, there are limited data available for 2010; therefore, we present in Figure 11 a comparison between the model output and the  $C_2H_6$  total column observations by using detrended and scaled data for the period of 2010–



2014 onto the year 2010 by using the same methodology and according to the annual rates of change reported by *Franco et al.* [2016]. This removes the effect of the observed  $C_2H_6$  decrease prior to 2009 and its increase from 2009 onward [*Franco et al.*, 2016]. For the Boulder site, the  $C_2H_6$  total column and GEOS-Chem model output comparison accounts for the altitude difference between the Boulder station and the coarse model grid cell, as explained in *Franco et al.* [2016]. The individual mixing ratio profiles from GEOS-Chem were regridded onto the vertical FTIR layer schemes by using a mass-conservative interpolation that preserves the total  $C_2H_6$  mass above the station altitude and ignores the mass underneath.

The model outputs for both  $C_2H_6$  emission inventories encompass the observed  $C_2H_6$  total columns. Compared to the 2001  $C_2H_6$  emission inventory, the  $C_2H_6$  total columns produced by the 2010 inventory stay almost all year round within a one standard deviation from the observations. Also, the 2010  $C_2H_6$  emission inventory produces a seasonality with broader maximum and minimum features that are in line with the observations.

## 5. Global Contribution of Fossil Fuel $C_2H_6$ Emissions to $O_3$ and PAN Mixing Ratios

Ethane is a precursor for both  $O_3$  and PAN. Because of its long lifetime and the resolution of our global simulations ( $2^\circ \times 2.5^\circ$ ), we estimate the contribution of  $C_2H_6$  fossil fuel sources to the global burden and surface mixing ratios of  $O_3$  and PAN rather than focus on specific oil and gas-producing regions. Our estimate is based on the comparison of a simulation without fossil fuel sources of  $C_2H_6$  to the results produced by using 2010  $C_2H_6$  emissions. The global contribution of fossil fuel  $C_2H_6$  emissions to  $O_3$  and PAN surface mixing ratios has a strong interhemispheric gradient. Due to the  $C_2H_6$  lifetime, which allows its transport to remote areas, the largest impacts on surface  $O_3$  and PAN occur over regions with low emissions of highly reactive hydrocarbons (Figures S2 and S3). The highest impacts on  $O_3$  and PAN surface concentrations occur over the Northern Hemisphere. For  $O_3$ , the highest contribution of fossil fuel  $C_2H_6$  emissions to surface mixing ratios is 0.58 ppbv during spring and summertime. Over land areas of the midlatitude Northern Hemisphere, fossil fuel  $C_2H_6$  emissions increase annual average  $O_3$  mixing ratios at the surface by 0.4 ppbv ( $\sim 1\%$ ). The effect is slightly smaller (0.3 ppbv) from  $50^\circ$  to  $70^\circ N$ . For PAN, the highest contributions to surface mixing ratios occur during spring (up to 30 pptv). Fossil fuel  $C_2H_6$  emissions enhance midlatitude Northern Hemisphere continental PAN mixing ratios up to 26 pptv, with an average contribution of  $\sim 8\%$  at the surface. The impacts of  $C_2H_6$  oxidation on atmospheric mixing ratios of  $O_3$  and PAN in the free troposphere are more homogeneous across all longitudes but similar in magnitude to the impacts near the surface. As  $C_2H_6$  emissions increase due to important fossil fuel sources like oil and natural gas activities, we anticipate greater contributions to both average mixing ratios of  $O_3$  and PAN. Given the similar emission totals between both  $C_2H_6$  emission inventories, our estimated contribution to global PAN annual burden is consistent with the *Fischer et al.* [2014] estimate of 6%, which was based on the *Xiao et al.* [2008]  $C_2H_6$  emission inventory implemented in GEOS-Chem v.9.01.01.

## 6. Conclusions

Due to recent and significant increases in the atmospheric  $C_2H_6$  burden, revisiting global  $C_2H_6$  emission inventories is needed. We update a global simulation of  $C_2H_6$  in the GEOS-Chem model by implementing a global  $C_2H_6$  emission inventory estimated from  $CH_4$  fluxes derived from satellite observations and a regional U.S. emission inventory derived by adjusting  $C_2H_6$  emissions from the NEI 2011 upward. We contrast two global  $C_2H_6$  emission inventories for the years 2001 and 2010. We show that these  $C_2H_6$  emission inventories have similar emission totals but very different spatial distributions. In particular, the distribution of emissions differs over the U.S., Europe, Russia, and the Middle East. Our 2010  $C_2H_6$  emission inventory, which includes  $C_2H_6$  emissions from 2010 satellite-derived  $CH_4$  fluxes and adjusted  $C_2H_6$  emissions from NEI 2011, produces  $C_2H_6$  emissions that are systematically larger over intense gas-producing regions and systematically lower over regions with low natural gas production compared to 2001  $C_2H_6$  emissions. Globally, the fossil fuel  $C_2H_6$  emissions in 2010 decrease by 0.8 Tg compared to 2001. This difference is consistent with the long-term global decline over this period ending in 2009 [*Franco et al.*, 2015; *Helmig et al.*, 2014a].

When compared to a suite of global observations of  $C_2H_6$ , the model simulations capture the  $C_2H_6$  seasonal cycle, the interhemispheric and vertical gradients, the surface mixing ratios, and the  $C_2H_6$  columns in most

regions. However, over some intensive natural gas production regions over the U.S., aircraft measurements reveal greater  $C_2H_6$  mixing ratios compared to the model, especially below 2 km. Given the reported strong increasing trend of the  $C_2H_6$  atmospheric burden that started in 2009 [Franco *et al.*, 2015; Helmig *et al.*, 2016] and an estimated increase of anthropogenic emissions in North America of 75% from 2008 to 2014 [Franco *et al.*, 2016], one plausible reason for this discrepancy could be the time difference between the measurements (2013–2014) and the 2010  $C_2H_6$  emissions implemented in the model. For these potentially fast-changing emission areas, large assumptions of continental or nationwide  $C_2H_6/CH_4$  emission ratios or emission inventory scaling are not likely to accurately represent the amount, distribution, and mixing ratio impacts of major local sources. Due to the limited observations and the scarcity of long-term in situ  $C_2H_6$  measurements within or downwind of oil and natural gas-producing regions, we recommend the use of different approaches to estimate  $C_2H_6$  emissions for a particular region/basin depending on the type of data available ( $CH_4/C_2H_6$  enhancement ratios, natural gas composition, etc.).

We found that fossil fuel  $C_2H_6$  emissions make the largest contributions to  $O_3$  and PAN over remote areas without large emissions of highly reactive hydrocarbons. Over continental areas in the Northern Hemisphere, we estimate an average increase of ~1% and ~8% to mean annual  $O_3$  and PAN surface mixing ratios, respectively, due to fossil fuel  $C_2H_6$  emissions. On a global scale, these results appear to be largely insensitive to the distribution of  $C_2H_6$  emissions over North America. These contributions from  $C_2H_6$  oxidation to  $O_3$  and PAN abundance are expected to be greater in 2014 compared to 2010 due to increased emissions from oil and natural gas extraction over the U.S. over this period [U.S. Environmental Protection Agency, 2015].

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