

1 Temporary pause in the growth of atmospheric ethane and 2 propane in 2015-2018

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14 Abstract.

15 Atmospheric non-methane hydrocarbons (NMHCs) play an important role in the formation of
16 secondary organic aerosols and ozone. After a multidecade global decline in atmospheric mole
17 fractions of ethane and propane – the most abundant atmospheric NMHCs – previous work has
18 shown a reversal of this trend with increasing atmospheric abundances from 2009 to 2015 in the
19 Northern Hemisphere. These concentration increases were attributed to the unprecedented growth
20 in oil and natural gas (O&NG) production in North America. Here, we supplement this trend
21 analysis building on the long-term (2008-2010; 2012-2020) high-resolution (~ 3-hour) record of
22 ambient air C₂-C₇ NMHCs from in-situ measurements at the Greenland Environmental
23 Observatory at Summit station (GEOSummit, 72.58  N, 38.48  W, 3210 m above sea level). We
24 confirm previous findings that the ethane mole fraction significantly increased by +69.0 [+47.4,
25 +73.2; 95 % confidence interval] ppt per year from January 2010 to December 2014. Subsequent
26 measurements, however, reveal a significant decrease by -58.4 [-64.1, -48.9] ppt per year from
27 January 2015 to December 2018. A similar reversal is found for propane. The upturn observed
28 after 2019 suggests, however, that the pause in the growth of atmospheric ethane and propane
29 might only have been temporary. Discrete samples collected at other northern-hemisphere baseline
30 sites under the umbrella of the NOAA cooperative global air sampling network show a similar

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37 decrease in 2015-2018 and suggest a hemispheric pattern. Here, we further discuss the potential
38 contribution of biomass burning and O&NG emissions, the main sources of ethane and propane,
39 and we conclude that O&NG activities likely played a role in these recent changes. This study,
40 highlights the crucial need for better constrained emission inventories.

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41 42 1. Introduction

43 Non-methane hydrocarbons (NMHCs) are emitted to the atmosphere by a variety of biogenic and
44 anthropogenic sources. Their atmospheric oxidation contributes to the production of surface ozone
45 and aerosols, with impacts on air quality and climate forcing (Houweling et al., 1998). The
46 abundance of atmospheric NMHCs (ethane, propane, i-butane, n-butane, i-pentane, n-pentane)
47 increased steadily after 1950 until reduced emissions from oil and natural gas (O&NG) production
48 and emission regulations from diverse sources (e.g., automobiles and industrial processes) were
49 implemented in the 1970s (Helmig et al., 2014). Emission reductions led to a gradual decline (3-
50 12 % per year) of NMHCs at urban and semi-rural sites in the last five decades (e.g., von
51 Schneidmesser et al., 2010; Warneke et al., 2012). Accounting for an approximate atmospheric
52 lifetime (at $\text{OH} = 6.5 \times 10^5$ molecules/cm³) ranging from 4.5 days for pentanes to 2 months for
53 ethane, these emission reductions are also reflected in observations of background air composition,
54 as seen in Northern Hemisphere firm air records (Aydin et al., 2011; Worton et al., 2012; Helmig
55 et al., 2014): light alkanes increased steadily post 1950, peaking ~50 % above 1950 levels around
56 1970-1985, and then steadily declined until 2010 to levels that were close to 1950 levels. After
57 some 40 years of steadily declining atmospheric ethane and propane mixing ratios, Helmig et al.
58 (2016) reported a reversal in this behavior: the analysis of weekly discrete air samples showed that
59 between mid-2009 and mid-2014, ethane abundance at surface sites in the Northern Hemisphere
60 increased at a rate of 2.9-4.7 % per year. These observations and conclusions were further
61 substantiated by solar Fourier transform infrared (FTIR) ethane column retrievals showing similar
62 increases in the mid to upper tropospheric ethane column (Franco et al., 2015, 2016; Hausmann et
63 al., 2016). The largest increase rates for ethane and propane mixing ratios were found at sites
64 located in the Eastern United States (U.S.) and in the Northern Atlantic Region, indicating larger
65 emissions from the central to eastern parts of the U.S., with the likely sources being increased
66 emissions from shale O&NG extraction operations.

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72 Interestingly, there is a strong latitudinal gradient of absolute NMHC dry air mole fractions – with
73 highest abundances in the Arctic where atmospheric removal rates are low during the polar winter
74 (Helmig et al., 2016, 2009; Rudolph, 1995). Despite the sensitivity of the Arctic to pollution
75 transport from lower latitudes, climate change, and already recognized and further anticipated
76 feedbacks on the global climate, long-term in-situ atmospheric composition observations within
77 the Arctic are sparse. A large part of our current knowledge of polar atmospheric chemistry stems
78 from research aircraft missions and campaign-type observations (e.g., Hartery et al., 2018; Jacob
79 et al., 2010; Law et al., 2014). However, long-term continuous measurements or regularly repeated
80 observations with consistent methodology and instrumentation are indispensable for establishing
81 a baseline record of environmental conditions at clean remote sites and for observing their changes
82 over time. Such data also serve as a legacy for future research that will rely on comparison with
83 archived observations of environmental conditions.

84 In that context, the National Oceanic and Atmospheric Administration (NOAA) Global
85 Monitoring Laboratory (GML) initiated a cooperative air-sampling network at Niwot Ridge,
86 Colorado, in 1967 (hereafter referred to as the NOAA/GML Carbon Cycle Greenhouse Gases
87 (CCGG) network (<https://www.esrl.noaa.gov/gmd/ccgg/>)). This network is nowadays an
88 international effort and discrete air samples are collected approximately weekly from a globally
89 distributed network of sites, including four Arctic sites: Utqiagvik (formerly known as Barrow,
90 Alaska, USA), Alert (Nunavut, Canada), Summit (Greenland), and Ny-Ålesund (Svalbard,
91 Norway). These samples are analyzed for CO₂, CH₄, CO, H₂, N₂O, and SF₆ at GML (e.g., Geller
92 et al., 1997; Komhyr et al., 1985; Steele, 1991), and at the University of Colorado Institute for
93 Arctic and Alpine Research (INSTAAR) for stable isotopes of CO₂ and CH₄ (Miller et al., 2002;
94 Troler et al., 1996). These samples have also been analyzed for a variety of volatile organic
95 compounds (VOCs) including C₂-C₇ NMHCs at INSTAAR since 2004 (Pollmann et al., 2008;
96 Schultz et al., 2015). In 2014, measurements of ethane and propane were added to discrete air
97 samples collected under the umbrella of the NOAA/GML Halocarbons and other Atmospheric
98 Trace Species (HATS) network since 2004
99 (<https://www.esrl.noaa.gov/gmd/hats/flask/flasks.html>).

100 The discrete, typically weekly, air sampling by cooperative global networks have been at the
101 forefront of studies to identify and quantify long-term trends in the background air abundances of
102 important trace gases (e.g., Masarie and Tans, 1995; Montzka et al., 2018; Nisbet et al., 2014,

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106 2019). In parallel, higher temporal-resolution in-situ measurements allow the investigation of
107 ~~gases' variability~~ and of shorter-term trends at specific sites. Here, we report in-situ 2 to 4-hourly
108 ambient air C₂-C₇ NMHCs dry air mole fractions from measurements at the Greenland
109 Environmental Observatory at Summit station (GEOSummit) by gas chromatography (GC) and
110 flame ionization detection (FID). Despite the advent of new methods based on optical
111 measurement (e.g., FTIR spectroscopy) and mass spectrometry (e.g., Photon-Transfer Mass
112 Spectrometry), GC-FID remains the dominant method in routine VOC observations due to its
113 stable long-term response characteristics and relatively low maintenance cost (Schultz et al., 2015).
114 NMHCs were first monitored with high temporal frequency at GEOSummit from 2008 to 2010
115 with support from the NASA Research Opportunities in Space and Earth Sciences (ROSES)
116 program (Kramer et al., 2015). NMHC monitoring resumed in 2012 as part of the National Science
117 Foundation (NSF) Arctic Observing Network program and ~~was~~ continuous and uninterrupted until
118 March 2020, providing one of the few high-temporal resolution long-term records of NMHCs in
119 the Arctic. In this paper, we investigate and discuss seasonal variations, rates of change, and
120 potential sources of NMHCs in the high Arctic. We also analyze multiyear trace gas data from
121 other background sites under the umbrella of the NOAA/GML CCGG and HATS sampling
122 networks to support our findings.

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124 2. Materials and Methods

125 GEOSummit (72.58°N, 38.48°W, 3210 m above sea level) is a research facility located on the
126 Greenland ice sheet funded by the U.S. NSF and operated in collaboration with the Government
127 of Greenland (see Fig. 1). The station hosts a diverse array of Geoscience and Astrophysics
128 research projects (<https://www.geosummit.org/instruments>) and is the only high altitude remote
129 atmospheric observatory in the Arctic. Ambient ~~air~~ is monitored at the Temporary Atmospheric
130 Watch Observatory (TAWO) ~~located~~ ~ 1 km south of the research camp.

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131 2.1 In-situ NMHC measurements

132 C₂-C₇ NMHCs (ethane, propane, iso-butane, n-butane, acetylene, iso-pentane, n-pentane, n-
133 hexane, benzene, toluene) were analyzed from July 2008 to July 2010 and from May 2012 to
134 March 2020 by GC-FID using a fully automated and remotely controlled custom-built system.
135 Ambient air was continuously sampled from a 10 m high inlet on the meteorological tower adjacent
136 to the TAWO building through a heated (~30°C) sampling line. The sampling frequency increased

142 from 6 ambient NMHC runs to 12 daily runs in 2018. The GC-FID system, tailored towards the
143 remote, unattended and long-term operation, is a further development of the instrument described
144 in detail by Tanner et al. (2006) and Kramer et al. (2015). The instrument relies on a cryogen-free
145 sample enrichment and injection system. Air was pulled from the tower inlet, and aliquots of the
146 sample stream were first passed through a water trap (u-shaped stainless-steel treated Silcosteel™
147 tube cooled using thermoelectric coolers) to dry the sample to a dew point of -20°C, and NMHCs
148 were then concentrated on a Peltier-cooled (-35°C) multi-stage adsorbent trap. Analysis was
149 accomplished by thermal desorption and injection onto an Al₂O₃ PLOT column for cryogen-free
150 separation on an SRI Model 8610 GC-FID. Our monitoring effort followed the World
151 Meteorological Organization (WMO) Global Atmospheric Watch (GAW) quality control
152 guidelines: blanks and calibration standards were injected every other day from the manifold and
153 processed in the exact same way as ambient samples. The limit of detection was ~2 ppt (pmol/mol
154 by volume) for all compounds and no significant blank contamination was ever noticed.
155 Quantification was based on monthly FID response factors (Scanlon and Willis, 1985) calculated
156 from the repeated analysis of two independently prepared and cross-referenced standards in use at
157 any given time. Tables S1 and S2 summarize these response factors along with the associated
158 relative standard deviation (< 5 % on average for all compounds) for 2008-2010 and 2012-2020,
159 respectively. The in-situ GC-FID system provided a stable response from 2008 to 2020, with
160 monthly response factors varying by ≤ 5 % for ethane, propane, and butanes, and by ≤ 20 % for
161 other compounds over this period. The monitoring program was audited by the World Calibration
162 Center for Volatile Organic Compounds at the site in July 2017 ([https://www.imk-ifu.kit.edu/wcc-](https://www.imk-ifu.kit.edu/wcc-voc/)
163 [voc/](https://www.imk-ifu.kit.edu/wcc-voc/)). All reported VOCs results were found to be within the Global Atmospheric Watch program
164 quality objectives (WMO, 2007).

165 2.2 Discrete measurements

166 We used NMHC data from Alert, Utqiagvik, Mace Head (Ireland), Park Falls (Wisconsin, USA),
167 and Cape Kumukahi (Hawaii, USA; see Fig. 1) collected as part of the NOAA/GML CCGG
168 (October 2004 to August 2016) and HATS (August 2014 to March 2020) sampling and
169 measurement programs. Note that we combined here measurements from the two networks.

170 2.2.1 CCGG discrete sampling and analysis

171 As described by Steele et al. (1987) and Dlugokencky et al. (1994), air samples are collected
172 ~weekly in pairs in 2.5 L borosilicate flasks with two glass-piston stopcocks sealed with Teflon

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174 O-rings. Flasks are flushed in series for 5 to 10 minutes ~~and~~ then pressurized to ~1.2 atm with a
175 portable sampling system. Samples collected from October 2004 to August 2016 were analyzed at
176 INSTAAR in Boulder, Colorado, by GC-FID. The analysis, on a HP-5890 series II gas
177 chromatograph, first involved drying of approximately 600 ~~cubic centimeter (cc)~~ of sample gas by
178 running the sample gas through a 6.4 mm ~~(outer diameter)~~ stainless steel tube cooled to -25°C.
179 The analytes were then preconcentrated at -35°C on an adsorbent bed (Carboxen 1000/1016).
180 Samples were thermally desorbed at 310°C onto a short capillary guard column before separation
181 on an Al₂O₃ PLOT capillary column (0.53 mm × 60 m). Weekly instrument calibrations were
182 performed using primary calibration standards acquired from the NOAA Global Monitoring
183 Laboratory, the U.K. National Physics Laboratory, and the U.S. National Institute of Technology.
184 These standards scales have been maintained since 2006 by regular inter-comparison ~~and~~
185 propagation of the scale with newly acquired standards. Deviations in the response factors from
186 these different standards were smaller than 5 %, with results for ethane and propane typically being
187 equal or having less than 2-3 % deviation. Instrument FID response is linear within the range of
188 observed ambient concentrations. The INSTAAR NMHC laboratory was audited by the WMO
189 GAW World Calibration Center for VOCs (WCC-VOC, <https://www.imk-ifu.kit.edu/wcc-voc/>) in
190 2008 and in 2016, and both times all measurement results passed the WMO data quality criteria
191 (WMO, 2007).

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192 2.2.2 HATS discrete sampling and analysis

193 At GEOSummit, paired borosilicate glass flasks are also pressurized to ~1 atmosphere
194 overpressure with ambient air as part of the HATS sampling program. At other NH sites,
195 electropolished stainless-steel flasks are used. All flasks are analyzed by GC with mass
196 spectrometry analysis with a preconcentration system similar to Miller et al. (2008) to strip water
197 vapor and CO₂ from the airstream prior to injection of condensates (VOCs, halocarbons, solvents,
198 and other gases) onto a 0.32 mm ~~(inner diameter)~~ GasPro capillary column. Results are tied to a
199 suite of standards prepared in-house with gravimetric techniques.

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200 2.3 Ancillary data

201 Continuous monitoring of carbon monoxide (CO) ~~was conducted~~ at GEOSummit ~~between~~ May
202 2019 ~~and March 2021~~ with a cavity ring-down spectroscopy (CRDS) analyzer (Picarro G-2401).
203 A switching manifold ~~allowed~~ regular sampling of ambient air and calibration gases. Three NOAA
204 GML standards were integrated into the automated calibration. Low (69.6 ppb) and high (174.6

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213 ppb) calibration points were performed for ~3 minutes every two days, while an intermediate
214 (117.4 ppb) calibration was carried out in between. Using the last minute of each calibration, the
215 low and high calibration points were used to determine the linear relationship between the certified
216 calibration values and the analyzer's reported calibration values. The calibration offset (slope and
217 intercept) was calculated and used to correct the third intermediate calibration point. The mean
218 absolute difference between the corrected and certified intermediate calibration paired values was
219 1.6 ppb, *i.e.*, 1.4 %. The minute-averaged CRDS CO ambient air data were corrected using the
220 calibration offset. The CRDS has a manufacturer-specified precision at 5 seconds, 5 minutes, and
221 60 minutes of 15, 1.5, and 1 ppb for CO (G2401 Gas Concentration Analyzer | Picarro, 2020).
222 We also use ethane, propane, tetrachloroethylene (C₂Cl₄), and hydrogen cyanide (HCN) data
223 collected in the free troposphere during the global-scale airborne Atmospheric Tomography
224 mission (ATom; <https://espo.nasa.gov/atom/content/ATom>) onboard the NASA DC-8 aircraft
225 (Wofsy et al., 2018). Canisters collected with the University of California Irvine Whole Air
226 Sampler (WAS) were analyzed for more than 50 trace gases, including ethane, propane, and
227 tetrachloroethylene by GC-FID and GC-mass spectrometric detection (Barletta et al., 2020).
228 Hydrogen cyanide was measured in situ with the California Institute of Technology Chemical
229 Ionization Mass Spectrometer (CIT-CIMS; Allen et al., 2019). For the purpose of our analysis, we
230 ~~removed~~ data collected over continents, in the marine boundary layer (altitude < 0.4 km), or
231 corresponding to stratospheric air (ozone to water vapor ratio > 1 ppb per ppm).

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232 **2.4 Curve fitting method and trend analysis**

233 We used the curve fitting method developed by Thoning et al. (1989) and described in detail at
234 <https://www.esrl.noaa.gov/gmd/ccgg/mb/krvfit/krvfit.html>. Briefly, the data were fitted with a
235 function consisting of a polynomial and series of harmonics to represent the average long-term
236 trend and seasonal cycle. Residuals from the function were calculated, transformed into frequency
237 domain with a fast Fourier transform algorithm, then filtered with two low pass filters. One
238 eliminates harmonics less than ~1 month. When converted back to time domain and added to the
239 function, it gives a smoothed curve. The other filter eliminates periods less than ~1 year; when
240 transformed back to time domain and added to the polynomial, it gives the deseasonalized trend
241 (hereafter referred to as the trend). The Sen's slope estimate of the trend was calculated using
242 function TheilSen in R package openair (Carslaw and Ropkins, 2012). Note that the p-values and

244 all uncertainties are calculated through bootstrap simulations
245 (<https://davidcarslaw.github.io/openair/reference/TheilSen.html>).

246 **2.5 Source apportionment analysis**

247 In order to identify potential source regions, we performed a Potential Source Contribution
248 Function (PSCF) analysis using the *trajLevel* function in R package openair (Carslaw and Ropkins,
249 2012). Based on air-mass back-trajectories (see below) and NMHC residuals (see Section 2.4), the
250 PSCF calculates the probability that a source is located at latitude i and longitude j . PSCF solves:

$$251 \quad PSCF = \frac{m_{ij}}{n_{ij}} \quad \text{Eq.1}$$

252 where n_{ij} is the number of times that the trajectories passed through the cell (i, j) and m_{ij} the
253 number of trajectories passing through that cell in which the NMHC residual was greater than a
254 given threshold (90th percentile of the measured results distribution). Note that cells with very few
255 trajectories passing through them have a weighting factor applied to reduce their effect.

256 For each NMHC in-situ measurement, HYSPLIT (HYbrid Single Particle Lagrangian Integrated
257 Trajectory; Draxler and Rolph, 2013) 5-day air-mass back trajectories used in the PSCF analysis
258 were generated using the Python package *pysplit* (Warner, 2018) and processor *pysplitprocessor*
259 available at: <https://github.com/brendano257/pysplit> and
260 <https://github.com/brendano257/pysplitprocessor>, respectively. The HYSPLIT Lagrangian
261 particle dispersion model was run from April 2012 to June 2019 using the National Center for
262 Environmental Prediction Global Data Assimilation System (NCEP GDAS) $0.5^\circ \times 0.5^\circ$
263 meteorological inputs available at: <ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas0p5>. We did not
264 generate back-trajectories for observations after June 2019 due to the unavailability of the GDAS
265 $0.5^\circ \times 0.5^\circ$ archive.

266

267 **3. Results and Discussion**

268 **3.1 Seasonal variation**

269 The seasonal variation of C₂-C₇ NMHCs at GEOSummit is displayed in Fig. 2. Summer refers to
270 June-August, fall to September-November, winter to December-February, and spring to March-
271 May. NMHCs exhibit a strong and consistent seasonal pattern year after year, with maximum mole
272 fractions during winter and early spring, and a rapid decline towards summer. Anthropogenic
273 sources of NMHCs do not vary much seasonally (Pozzer et al., 2010). Therefore, the observed
274 seasonal cycle is primarily driven by the seasonally changing sink strength by reaction with the

275 photochemically formed OH radical (Goldstein et al., 1995) – the dominant oxidizing agent in the
276 global troposphere (Levy, 1971; Logan et al., 1981; Thompson, 1992). During the summer period,
277 mole fractions of the heavier NMHCs were below or close to the detection limit (Fig. 2b). As
278 already noted by Goldstein et al. (1995) and Kramer et al. (2015) based on a limited dataset, the
279 phase of each NMHC is shifted due to the rate of reaction with OH. Ethane, the lightest and longest
280 lived of the NMHCs shown in Fig. 2, peaks in February/March with a median of 2110 ppt, and
281 declines to a minimum of 734 ppt in July. Heavier and shorter-lived NMHCs have lower mole
282 fractions, peak earlier in the year (January/February), and reach a minimum earlier in summer
283 (June) due to their faster rate of reaction with OH (Chameides and Cicerone, 1978).
284 Because changes in NMHC sources and sinks can affect the seasonal cycle amplitude, we
285 investigated whether there is a trend in the NMHC's amplitude at GEOSummit. We focus here on
286 ethane and propane, the most abundant hydrocarbons in the remote atmosphere after methane.
287 Figure 3 shows the amplitude of the ethane and propane seasonal cycles, determined as the relative
288 difference between the maximum and minimum values from the smooth curve for each annual
289 cycle (Dlugokencky et al., 1997). The peak-to-minimum relative amplitude ranged from 64 to 71
290 % for ethane and from 92 to 96 % for propane, and there is no indication of a significant overall
291 trend in amplitude. This range of amplitudes is in good agreement with the literature: the typical
292 seasonal amplitudes for ethane are on the order of 50 % at mid-latitude sites and can increase up
293 to 80 % at remote sites (Franco et al., 2016; Helmig et al., 2016). Changes in mole fractions are
294 further investigated and discussed in the following section.

295 3.2 Reversal of ethane and propane rates of change at GEOSummit in 2015

296 Ethane is released from seepage of fossil carbon deposits, volcanoes, fires, and from human
297 activities – with O&NG extraction, processing, distribution, and industrial use being the primary
298 sources (Pozzer et al., 2010). Based on the inventory developed for the Hemispheric Transport of
299 Air Pollutants, Phase II (HTAP2, Janssens-Maenhout et al., 2015), biogenic emissions from
300 MEGAN2.1 (Guenther et al., 2012), and fire emissions from FINNv1.5 (Wiedinmyer et al., 2011),
301 Helmig et al. (2016) estimated that ~4 %, 18 %, and 78 % of global ethane emissions are due to
302 biogenic, biomass burning, and anthropogenic sources, respectively. Global ethane emission rates
303 decreased by 21 % from 1984 to 2010 likely due to decreased venting and flaring of natural gas in
304 oil producing fields (Simpson et al., 2012). As a consequence, atmospheric ethane background air
305 mixing ratios significantly declined during 1984-2010, by an average of -12.4 ± 1.3 ppt per year

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311 in the Northern Hemisphere (Aydin et al., 2011; Worton et al., 2012; Helmig et al., 2014).
312 However, the analysis by Helmig et al. (2016) of ten years (2004-2014) of NMHC data from air
313 samples collected at NOAA GML remote global sampling sites (including GEOSummit) showed
314 a reversal of the global ethane trend from mid-2009 to mid-2014 (ethane growth rates > 50 ppt per
315 year at 32 sites). This trend reversal was attributed to increased U.S. O&NG production (Helmig
316 et al., 2016). Figure 4a shows the July 2008-March 2020 ethane trend at GEOSummit, as inferred
317 from our in-situ measurements (dotted line). Note that the same time-series but also showing
318 individual data points can be found in Fig. S1. Ethane mixing ratios at GEOSummit significantly
319 (p-value < 0.001) increased by +69.0 [+47.4, +73.2; 95 % confidence interval] ppt per year from
320 January 2010 to December 2014. A reversal is, however, evident after 2015: ethane mixing ratios
321 significantly (p-value < 0.001) decreased by -58.4 [-64.1, -48.9] ppt per year from January 2015
322 to December 2018. Data collected after 2019, however, suggest that the pause in the growth of
323 atmospheric ethane might only be temporary. We focus hereafter on the 2015-2018 reversal period.
324 Similar to ethane, a reversal is evident late 2014 for propane (see Fig. 4b; dotted line): mixing
325 ratios significantly (p-value < 0.001) increased by +47.9 [+32.3, +52.3] ppt per year from January
326 2010 to June 2014, but significantly (p-value < 0.001) decreased at a rate of -70.5 [-76.1, -65.8]
327 ppt per year from July 2014 to July 2016. Propane mixing ratios remained fairly stable (+10.2
328 [+6.6, +14.6] ppt per year; p-value < 0.001) from July 2016 to December 2019. It should be noted
329 that the pause in the growth of atmospheric ethane and propane at GEOSummit in 2015-2018 is
330 confirmed by independent discrete sampling under the umbrella of the NOAA/GML CCGG and
331 HATS networks (see Fig. 4; solid lines). Figure S2 shows the good agreement ($R^2 = 0.97$ for
332 ethane, $R^2 = 0.99$ for propane) between in-situ GC-FID measurements and discrete samples.
333 The temporary pause in the growth of ethane and propane at GEOSummit could either suggest
334 changes in: i) the OH sink strength, ii) atmospheric transport from source regions and/or iii)
335 natural/anthropogenic emissions.
336 The tropospheric abundance of OH is driven by a complex series of chemical reactions involving
337 tropospheric ozone, methane, carbon monoxide, NMHCs, and nitrogen oxides, and by the levels
338 of solar radiation and humidity (Logan et al., 1981; Thompson, 1992). Building on the comparison
339 of modeled and observed methane and methyl chloroform lifetimes, Naik et al. (2013) showed that
340 OH concentrations changed little from 1850 to 2000. The authors suggested that the increases in
341 factors that enhance OH (humidity, tropospheric ozone, nitrogen oxide emissions, and UV

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346 radiation) was compensated by increases in OH sinks (methane abundance, carbon monoxide and
347 NMHC emissions). More recently, Naus et al. (2020) used a 3D-model inversion of methyl
348 chloroform to constrain the atmospheric oxidative capacity – largely determined by variations in
349 OH – for the period 1998-2018. The authors showed that the interannual variations were typically
350 small (<3 % per year) and found no evidence of a significant long-term trend in OH over the study
351 period. Changes in NMHC mole fractions at GEOSummit are well outside what could be explained
352 by a 3% change in OH tropospheric concentrations. There is, however, likely a difference between
353 global and regional OH variations (Brenninkmeijer et al., 1992; Spivakovsky et al., 2000;
354 Lelieveld et al., 2004). In the absence of data on the Arctic and mid-latitudes OH abundance, we
355 concede that OH may play a role on the observed pause but do not discuss that hypothesis further.
356 The latter two hypotheses are investigated and verified or rejected in the following sections.

357 3.3 Changes in transport from source regions

358 The synoptic-scale tropospheric circulation in the Arctic is driven by three major semi-permanent
359 pressure systems: i) the Aleutian Low, low-pressure center located south of the Bering Sea area,
360 ii) the Icelandic Low, low-pressure system located southeast of Greenland near Iceland, and iii)
361 the Siberian High, high-pressure center located over eastern Siberia (Barrie et al., 1992). During
362 positive phases of the North Atlantic Oscillation (NAO), the Icelandic Low is strengthened and
363 transport into the Arctic enhanced, resulting in higher Arctic pollution levels (Duncan and Bey,
364 2004; Eckhardt et al., 2003). Negative phases of the NAO are associated with decreased transport
365 from Europe and Siberia and an increased relative contribution from North America (Octaviani et
366 al., 2015). In addition, mid-latitude atmospheric blocking events – quasi-stationary features
367 characterized by a high-pressure cell centered around 60°N and lasting up to ~15 days (Rex, 1950)
368 – are known to enhance transport of polluted air to the Arctic (Iversen and Joranger, 1985). Here,
369 we test the hypothesis of a pause in the growth of atmospheric ethane and propane at GEOSummit
370 driven by the interannual variability of pollution transport from source regions. We investigated
371 the potential influence of the NAO using monthly mean values from the NOAA Climate Prediction
372 Center. We found a somewhat weak but significant positive correlation between the NAO and
373 monthly-averaged mixing ratios over the 2008-2019 period ($R^2 = 0.4$, $p\text{-value} < 0.01$ for both
374 ethane and propane), in line with enhanced transport of pollution to the Arctic during positive
375 phases of the NAO. We also investigated the potential influence of the Northern Annular Mode
376 (NAM), which has a strong interannual component (Hu and Feng, 2010). We found a low

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380 correlation between the NAM and monthly-averaged mixing ratios ($R^2 < 0.2$, p-value = 0.1 for
381 both ethane and propane). Previous studies have shown that the influence of the NAM varies by
382 regional section of the Arctic; while persistent organic pollutants concentrations were found to
383 correlate with NAM phases at Ny-Ålesund (Svalbard), no correlation was found at Alert (Nunavut,
384 Canada) (Becker et al., 2008; Octaviani et al., 2015).

385 Figure 5 shows the origin of air masses influencing GEOSummit (annual gridded back trajectory
386 frequencies) and Figure 6a summarizes the relative contribution of each geographical sector for
387 each year. Contrary to other Arctic sites (Hirdman et al., 2010), GEOSummit is mostly influenced
388 by transport from North America and Europe, whereas Siberia has relatively little influence (0-2
389 %). These results are in agreement with the isobaric 10-day back-trajectory study by Kahl et al.
390 (1997) and the 20-day backward FLEXPART simulations by Hirdman et al. (2010). European air
391 masses represented 3-6 % of the total, with a 10 % high in 2018. The relative contribution of North
392 Atlantic air masses (“ocean”) ranged from 1 to 9 %, with a 14 % high from January to August
393 2019. The frequency of North American air masses exhibited the most variability, ranging from 2
394 to 20 %. Years with enhanced transport from North America (e.g., 2012, 2019) coincided with a
395 negative NAO index, known to drive decreased (increased) relative contribution from Europe/Asia
396 (North America) (Octaviani et al., 2015). Assuming that the ethane and propane trends are driven
397 by emissions in North America (Helmig et al., 2016) and that these emissions are constant, one
398 would expect higher ethane and propane mixing ratios in years when the relative influence of
399 North American air masses peaked. There is, however, an anticorrelation: a 2-3 % relative
400 contribution of North American air masses in 2014 and 2015 when ethane/propane mixing ratios
401 reached a maximum, and 19 % in 2018 when mixing ratios reached a minimum. This leaves two
402 possibilities: either North American emissions dropped over the studied time period (see Section
403 3.4), or ethane/propane trends observed at GEOSummit are not driven by emissions in North
404 America (see below).

405 The relative contribution of local/regional air masses (i.e., around Greenland, see Fig. 5) increased
406 from 79 % in 2012 to 91-93 % in 2014-2015 before gradually dropping to 61 % in 2018. The
407 apparent correlation between the relative contribution of local/regional air masses and the
408 ethane/propane trend raises the question of whether these are connected. In order to identify
409 potential sources in this sector, we performed a PSCF analysis to investigate source-receptor
410 relationships (e.g., Pekney et al., 2006; Perrone et al., 2018; Yu et al., 2015; Zhou et al., 2018;

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Deleted: Local/regional air masses (i.e., around Greenland, see Fig. 5) were the most frequently impacting the site (located near the receptor site). Interestingly,

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421 Zong et al., 2018). The PSCF calculates the probability that a source is located at latitude i and
422 longitude j (Pekney et al., 2006). Figure S3 shows the results of the PSCF analysis for ethane and
423 propane residuals and shows no consistent pattern associated with elevated concentrations. In both
424 winter and summer, the probability of an ethane or propane source from this analysis is low (<2
425 % on average).

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426 The history of petroleum exploration activities on the Greenland continental shelf dates back to
427 the 1970s (Arctic Oil & Gas Development: The Case of Greenland, 2020). More recently, the
428 Greenland's government announced the opening of three new offshore areas for exploration in
429 November 2020 (Greenland Opens Offshore Areas for Drilling, 2020). Despite exploration drilling
430 activities, there has never been any O&NG exploitation of Greenland resources (Arctic Oil &
431 Gas Development: The Case of Greenland, 2020). Building on the above, the possibility of a
432 significant local/regional source can be ruled out, and so can the hypothesis that the pause in the
433 growth of ethane and propane is driven by local/regional emissions. The last remaining hypothesis
434 is that this pause is due to a change in emissions from any of the other source sectors, or a
435 combination of them, or total NH emissions and associated change in baseline NH atmospheric
436 levels. This hypothesis is tested in the following Section using observations at other baseline sites.

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437 3.4 Evidence for a hemispheric pattern

438 Table 1 summarizes the rate of change and 95 % confidence interval for 2010-2014 and 2015-
439 2018 at Alert (ALT, Nunavut, Canada), Utqiagvik/Barrow (BRW, Alaska, USA), Cape Kumukahi
440 (KUM, Hawaii, USA), Park Falls (LEF, Wisconsin, USA), and Mace Head (MHD, Ireland – see
441 Fig. 1) where discrete samples were collected for the NOAA/GML CCGG and HATS cooperative
442 networks. The ethane and propane time-series at the various sites are shown in Figures S4 and S5,
443 respectively. A clear reversal in interannual changes for ethane and propane mixing ratios is
444 observed in 2015 at ALT, BRW, KUM, and LEF. These results support the observed changes at
445 GEOSummit and indicate a hemispheric pattern, likely due to a change in Northern Hemisphere
446 emissions, with a turning point around late 2014. Biomass burning and anthropogenic activities
447 being the main emitters of NMHCs, we hereafter focus the discussion on these two sources.

448 3.4.1 Biomass burning

449 Occasional biomass burning plumes were observed at GEOSummit. For example, Fig. 7 shows
450 the simultaneous increase in CO, ethane, propane, and benzene mixing ratios for a short number
451 of days in July and August 2019. According to the Whole Atmosphere Community Climate Model

454 (WACCM; Gettelman et al., 2019) CO forecast simulations, available at
455 <https://www.acom.ucar.edu/wacm/forecast/>, these enhancements can be attributed to intense
456 Siberian wildfires occurring at that time (Bondur et al., 2020). In good agreement with the
457 WACCM simulations, emission ratios (amount of compound emitted divided by that of a reference
458 compound) derived from these two plumes for ethane and propane ($5.4\text{-}5.9 \times 10^{-3}$ and $1.5\text{-}1.6$
459 $\times 10^{-3}$ ppb per ppb of CO, respectively; see Fig. S6) are within the range of values reported for
460 boreal forest and peat fires (Andreae, 2019).

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461 Despite the observation of occasional plumes at GEOSummit, the question remains whether
462 biomass burning could drive the observed hemispheric pause in the growth of atmospheric ethane
463 and propane. For ethane, the sensitivity to biomass burning emissions from boreal fires is almost
464 entirely balanced by the larger magnitude of emissions from non-boreal fires (Nicewonger et al.,
465 2020). For propane, being shorter-lived, the fire component over Greenland should be dominated
466 by emissions from boreal fires. We thus investigated the interannual variability of biomass burning
467 emissions from both all open burning north of 45°N (boreal fires) and north of the equator (all NH
468 fires). Figure 6b gives annual biomass burning emissions according to the Fire INventory from
469 NCAR (FINNv2.2) emission estimates driven by MODIS fire detections (Wiedinmyer et al., in
470 prep). Emissions north of 45°N peaked in 2012, known for being an exceptional wildfire season
471 in North America (e.g., Lassman et al., 2017; Val Martin et al., 2013). NH ethane and propane
472 emissions slightly decreased in 2017 and 2018 but were fairly stable over the 2008-2016 time
473 period. We did not find any significant correlation between annual biomass burning emissions and
474 annually-averaged mixing ratios (using either 2009-2018 or 2015-2018 data, and using either all
475 open burning north of 45°N or north of the equator). The seasonal analysis of the correlation
476 between ambient air mixing ratios and biomass burning emissions yielded similar results. This
477 suggests that the observed pause in the growth of atmospheric ethane and propane is likely not
478 driven by biomass burning emissions.

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479 This conclusion is further supported by measurements during the aircraft mission ATom over the
480 Pacific and Atlantic Oceans. Using ethane and propane data collected in the Northern Hemisphere
481 ($>20^\circ\text{N}$) remote free troposphere during the four ATom seasonal deployments (July-August 2016,
482 January-February 2017, September-October 2018, and April-May 2018), we found a significant
483 positive correlation of ethane and propane with tetrachloroethylene ($R^2 = 0.6$, $p\text{-value} < 0.001$) and
484 a poor correlation with hydrogen cyanide ($R^2 < 0.1$, $p\text{-value} < 0.001$; see Fig. S7), used as tracers

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497 of anthropogenic and biomass burning emissions, respectively (Bourgeois et al., in review). These
498 results from the remote free troposphere confirm that atmospheric ethane and propane ambient air
499 levels are mostly driven by anthropogenic activities rather than by biomass burning emissions, in
500 line with results from other studies (e.g., Xiao et al., 2008).

501 3.4.2 O&NG activities

502 Discrete samples collected at northern-hemisphere baseline sites show that the strongest change
503 was observed at LEF, located downwind from the Bakken oil field in North Dakota (Gvakharia et
504 al., 2017), with an increase of ethane mixing ratios of +167.7 [+157.5, +186.0] ppt per year in
505 2010-2014 and a decrease of -247.8 [-312.2, -158.2] ppt per year in 2015-2018 (see Table 1). This
506 result, along with previous findings by Helmig et al. (2016) and Franco et al. (2015), supports the
507 hypothesis that U.S. O&NG emissions could play a major role in driving atmospheric ethane and
508 propane concentrations in the NH. Here we further discuss this potential contribution to the
509 observed hemispheric pause in the growth of atmospheric ethane and propane in 2015-2018.

510 The U.S. has experienced dramatic increases in O&NG production since 2005, underpinned by
511 technological developments such as horizontal drilling and hydraulic fracturing (Caporin and
512 Fontini, 2017; Feng et al., 2019). This shale revolution has transformed the U.S. into the world's
513 top O&NG producer (Gong, 2020). Coincident with the shale gas boom, the U.S. production of
514 natural gas liquids (ethane, propane, butane, iso-butane, and pentane) has significantly increased
515 in the past decade from 0.6-0.7 billion barrels in the 2000s to 1.1 billion barrels in 2014, and close
516 to 1.8 billion barrels in 2019 (U.S. Field Production of Natural Gas Liquids, 2021). ~~The main~~
517 ~~source of ethane and propane has been identified to be leakage during the production, processing,~~
518 ~~and transportation of natural gas (Tzompa-Sosa et al., 2019; Pétron et al., 2012; Roest and Schade,~~
519 ~~2017).~~

520 Propane is extracted from natural gas stream and used as a heating fuel. As shown in Figure 8, the
521 U.S. propane field production temporarily plateaued from June 2014 to December 2016 (U.S. Field
522 Production of Propane, 2021) due to a slowdown in natural gas production in response to low
523 natural gas prices. As we consider recent changes in emissions, however, changes in emissions per
524 unit of production must also be considered. A recent study in the Northeastern Colorado Denver-
525 Julesburg Basin showed little change in atmospheric hydrocarbons, including propane, in 2008-
526 2016 despite a 7-fold increase in oil production and nearly tripling of natural gas production,
527 suggesting a significant decrease in leak and/or venting rate per unit of production (Oltmans et al.,

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531 2021). While we cannot reliably estimate how propane emissions might have changed during this
532 recent period, these two influences, combined together, could explain the observed temporary
533 pause in the growth of atmospheric propane.

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534 Estimating the total production, and ultimately emissions, of ethane, is even more complex as it
535 depends on the ethane-to-natural gas price differential. Ethane has long been considered an
536 unwanted byproduct of O&NG drilling, much of it burned away in the natural gas stream or flared
537 off at well sites. Today, ethane is a key feedstock for petrochemical manufacturing and the U.S. is
538 currently the world's top producer and exporter of ethane (Sicotte, 2020). Depending on the price
539 of ethane relative to natural gas, ethane can be left in the natural gas stream and sold along with
540 natural gas – a process known as ethane rejection, or separated at natural gas processing plants
541 along with other natural gas liquids (such as propane). Assuming the same leak rates for ethane as
542 for methane, 85 % of ethane emissions are due to natural gas extraction and processing, while
543 processed natural gas transportation and use only represent 15 % of the natural gas supply chain
544 ethane loss rate (Alvarez et al., 2018). The slowdown in natural gas production from June 2014 to
545 December 2016 (see above) may thus have contributed to the atmospheric ethane plateauing.
546 However, these estimates do not take into account emissions of ethane from its own supply chain
547 (e.g., separation, storage, liquefaction for export, ethane cracker to produce ethylene and plastic
548 resins) – for which leak rates remain unknown. A number of top-down studies, focusing on specific
549 regions or time-periods (e.g., 2010-2014), have shown that current inventories underestimate
550 ethane emissions (e.g., Tzompa-Sosa et al., 2017; Pétron et al., 2014). The modeling study led by
551 Dalsøren et al. (2018) focusing on year 2011 claimed that fossil fuel emissions of ethane are likely
552 biased-low by a factor of 2-3. In this highly dynamic context, where ethane production and volume
553 rejected continuously vary and where leak rates change over time (Schwietzke et al., 2014), there
554 is a need for further hemispheric- or global-scale top-down studies focusing on the interannual
555 variability of ethane emissions.

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557 4. Summary and Conclusion

558 Ethane and propane are the most abundant atmospheric NMHCs and they exert a strong influence
559 on tropospheric ozone, a major air pollutant and greenhouse gas. Increasing levels have been
560 reported in the literature from 2009 to 2014, with evidence pointing at U.S. O&NG activities as
561 the most likely cause (Kort et al., 2016; Helmig et al., 2016; Franco et al., 2016; Hausmann et al.,

565 2016). The long-term high-resolution records of ambient air C₂-C₇ NMHCs at GEOSummit
566 presented here confirm that atmospheric ethane and propane levels increased in the remote arctic
567 troposphere from 2009 to 2015, but also reveal a pause in their growth in 2015-2018. Using
568 independent discrete samples collected at other NH baseline sites, we show that this pause is
569 observed throughout the northern hemisphere – suggesting a change in total NH emissions and in
570 baseline NH atmospheric levels. We further investigated and discussed the contribution of the two
571 main NMHC emitters: biomass burning and O&NG production. We did not find any correlation
572 between atmospheric ethane and propane mixing ratios and the FINNv2.2 biomass burning
573 emission estimates. Additionally, data collected in the NH remote free troposphere during the
574 ATom aircraft campaign support that atmospheric ethane and propane ambient air levels are
575 mostly driven by anthropogenic activities rather than by biomass burning emissions. The fact that
576 the strongest rate of change reversal was observed at a site located downwind from the Bakken oil
577 field in North Dakota tends to suggest that U.S. O&NG activities yet again played a major role
578 here. The slowdown in U.S. natural gas production from June 2014 to December 2016 combined
579 with a decrease in leak rate per unit of production could have contributed to the observed temporary
580 pause. This conclusion is, however, tentative given the large uncertainties associated with emission
581 estimates, especially with ethane emissions from its supply chain. We hope this work can be used
582 as a starting point to understand what led to the pause in the growth of atmospheric ethane and
583 propane in 2015-2018 and, more generally, to what extent ON&G activities could be responsible
584 for variations in NH baseline ethane and propane levels.

Deleted: The analysis of air-mass back-trajectories allowed us to rule out the possibility that this pause is driven by a change in transport from source regions.

585 586 **Data availability**

587 All non-methane hydrocarbons and carbon monoxide in-situ data used in this study are archived
588 and publicly available on the Arctic Data Center database (Angot et al., 2020; Helmig, 2017).
589 NOAA/GML HATS and CCGG discrete data are available at
590 <ftp://aftp.cmdl.noaa.gov/data/hats/PERSEUS> and ftp://aftp.cmdl.noaa.gov/data/trace_gases/voc/,
591 respectively.

592 593 **Author contribution**

594 DH initiated the long-term monitoring effort at GEOSummit and secured funding over the years.
595 JH designed and built the GC-FID used for NMHC in-situ monitoring and performed ~bi-annual

599 on-site visits for maintenance and calibration operations. CD, JC, and BB performed the in-situ
600 data processing (*i.e.*, GC peak identification, peak integration, background subtraction, and
601 calculation of mixing ratios). CD, JC, and HA analyzed the data under the supervision of CW and
602 DH. GP helped evaluating the impact ON&G activities on NMHC trends while IB and CW helped
603 evaluating the impact of biomass burning. IV, SAM, BRM and JWE provided the NOAA /GML
604 HATS discrete data. JH and DH provided the NOAA/GML CCGG NMHC discrete data with
605 contribution from CD, JC, and BB. HA wrote the manuscript with contribution from all co-authors.
606

607 **Competing interests**

608 The authors declare no competing interests.
609

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628

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