Methane and ethane are the most abundant hydrocarbons in the atmosphere and they affect both atmospheric chemistry and climate. Both gases are emitted from fossil fuels and biomass burning, whereas methane (CH₄) alone has large sources from wetlands, agriculture, landfills and waste water. Here we use measurements in firn (perennial snowpack) air from Greenland and Antarctica to reconstruct the atmospheric variability of ethane (C₂H₆) during the twentieth century. Ethane levels rose from early in the century until the 1980s, when the trend reversed, with a period of decline over the next 20 years. We find that this variability was primarily driven by changes in ethane emissions from fossil fuels; these emissions peaked in the 1960s and 1970s at 14–16 teragrams per year (1 Tg = 10¹² g) and dropped to 8–10 Tg yr⁻¹ by the turn of the century. The reduction in fossil-fuel sources is probably related to changes in light hydrocarbon emissions associated with petroleum production and use. The ethane-based fossil-fuel emission history is strikingly different from bottom-up estimates of methane emissions from fossil-fuel use1,4, and implies that the fossil-fuel source of methane started to decline in the 1980s and probably caused the late twentieth century slow-down in the growth rate of atmospheric methane3,4.

Ethane is an organic trace gas that is primarily emitted to the atmosphere during mining, processing, transport and consumption of fossil fuels, during use of biofuels, and during biomass burning4–6. It acts as a precursor of ozone and carbon monoxide in the troposphere. Ethane is oxidized rapidly by the hydroxyl radical (OH) and has a seasonally varying lifetime (annual mean ~2 months). The short lifetime, coupled with a north–south asymmetry in its sources, leads to geographic and temporal variability in its atmospheric abundance5,7. Ethane abundance displays strong seasonal variability, with peak-to-peak amplitudes comparable to annual-mean levels. Annual-mean ethane levels are highest at high northern latitudes (HNL, that is, 30–90° N; 1.5 parts per billion) and lowest at high southern latitudes (HSL, that is, 30–90° S; 250 parts per trillion)4.

We measured ethane in firn air collected at Summit (in Greenland), at the West Antarctic Ice Sheet – Divide, WAIS-D (in Antarctica), and at the South Pole. A synthesis inversion method was used to develop atmospheric histories of ethane for each site, using a one-dimensional firn air diffusion model (Fig. 1) (see Methods Summary). The mean temperatures and the ice accumulation rates are very similar at Summit (−31 °C, 20 cm yr⁻¹) and at WAIS-D (−31 °C, 22 cm yr⁻¹), resulting in similar gas age distributions in the firn and atmospheric histories constrained for the past 50–60 years (refs 8, 9). South Pole is considerably colder (−51 °C), with a lower ice accumulation rate (−8 cm yr⁻¹) and a deeper firn column. As a result, atmospheric histories based on South Pole firn air measurements are constrained for the past 80–90 years (ref. 10). The ethane atmospheric histories based on the WAIS-D and South Pole firn air measurements display the same trends for the period since 1950 (Fig. 1).

Mean annual ethane levels measured over Summit and South Pole are consistent with those at other high-latitude sites, indicating that the

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**Figure 1** Ethane mixing ratios in firn air at three sites, and the atmospheric histories derived from these measurements. a–f. Results for Summit (a, b, South Pole (c, d) and WAIS-D (e, f). Filled and open squares in a, c and e show measurements with estimated uncertainties (error bars, ±2 s.e.) (Supplementary Data). Solid lines in a, c and e show modelled firn profiles for the three respective sites, with the five different atmospheric histories (solid lines) shown in b, d and f. These five atmospheric histories were obtained by inverse modelling of the measurements with five different boundary conditions at t₀, that are identified by different colours, each representing a different pre-industrial mixing ratio for ethane. The data points in the top 35 m (Summit and South Pole) and 40 m (WAIS-D) of the firn are subject to the effects of seasonal variations in surface ethane levels (Supplementary Information) and are ignored during inverse modelling (open squares in a, c and e). The inversions were forced with contemporary annual-mean surface mixing ratios of 1,460 p.p.t. at Summit and 215 p.p.t. at South Pole and WAIS-D (red triangles in a, c and e) (Supplementary Information). The South Pole atmospheric history is overlaid on the independently derived WAIS-D atmospheric histories for comparison (dashed line in f). The inversions are sensitive to assumptions about the pre-industrial ethane levels before 1950, 1940 and 1910 at Summit, WAIS-D and South Pole, respectively (shaded areas), implying that only the inversion results for the later years are valid atmospheric histories.
measurements in polar firm air provide a reasonable sampling of the ethane mixing ratios in high latitudes (see Supplementary Information). Together, the three atmospheric histories show ethane levels peaking in the HNL and HSL atmospheres in the early 1980s, followed by a decline over the 20 years that followed. The South Pole site contains sufficiently old air to constrain the ramp-up period during the early to mid twentieth century (Fig. 1). On the basis of these atmospheric histories, HSL annual-mean ethane levels increased fivefold between 1910 and 1980 (from about 60 p.p.t. to 280 p.p.t.), and declined more than 10% (to less than 250 p.p.t.) by 2000. In the HNL, ethane increased from ~1.7 p.p.b. in 1950 to ~2.0 p.p.b. in 1980, and declined 25% to ~1.5 p.p.b. in 2000.

To infer the causes of the atmospheric ethane variations in terms of changes in large-scale sources, we must relate high-latitude ethane levels to hemispheric averages. We used the modern atmospheric ethane distribution and sensitivity tests with the UCI Chemical Transport Model (UCI-CTM) to derive ratios relating the response of the HNL and HSL to changes in hemispheric mean ethane levels (see Supplementary Information). Next, we used a simple two-box model (see Methods Summary) representing the troposphere in the Northern and Southern hemispheres to simulate variations in mean atmospheric ethane levels over the past century resulting from various scenarios for fossil-fuel, biomass-burning, and biofuel emissions. Fossil-fuel and biofuel emissions are concentrated in the northern mid-latitudes, and biomass burning in the tropics. As a result, these sources contribute to hemispheric ethane levels with different efficiencies (see Methods Summary and Supplementary Information).

The two-box model was used to infer the fossil-fuel ethane emission histories needed to achieve agreement with the firm-air-derived atmospheric ethane histories from Summit and South Pole, under various assumptions about biomass-burning emissions (Fig. 2, see Supplementary Information). The results show clearly that ethane variability over decadal timescales during the twentieth century was dominated by changes in the fossil-fuel ethane source. When biomass-burning and fossil-fuel ethane emissions are both allowed to vary after 1950, the model yields a biomass-burning source of less than 1 Tg yr\(^{-1}\) in 1950, rising to ~3 Tg yr\(^{-1}\) by 2000, followed by a drop to 2 Tg yr\(^{-1}\) in 1950s. Fossil-fuel emissions are then constant for about 20 years, followed by a 45% drop over the next 30 years. The model yields 8–10 Tg yr\(^{-1}\) for fossil-fuel ethane emissions at the end of the twentieth century, consistent with the modern ethane budget inferred from atmospheric ethane levels.

Fossil-fuel emissions are also a significant source of methane into the atmosphere, and the observed decline in the growth rate of atmospheric methane parallels the decline in atmospheric ethane levels during 1980–2000. This evidence suggests that the decline in methane growth rates was caused by a gradual reduction in fossil-fuel emissions, which was already underway when continuous direct atmospheric measurements of methane started in 1984 and 1985. The stabilization of atmospheric methane in recent years (also see Supplementary Information) suggests that fossil-fuel emissions are now steady. Thus, the recent increases in atmospheric methane levels are probably not derived from increased fossil-fuel emissions and must be due to other sources, as previously suggested.

The ethane-based biomass-burning emission history agrees well with some independent estimates. However, our fossil-fuel emissions history is quite different from bottom-up methane emission inventories (Fig. 3). Most notably, the ethane-based fossil-fuel emissions display a steep ramp-up after 1920 and a sharp decline after 1980, whereas the bottom-up methane fossil-fuel emission inventories display a generally increasing trend through the entire twentieth century, with the sharpest increases occurring between 1950 and 1980. Hydrocarbons are emitted from a variety of fossil-fuel sources, each exhibiting a different range of methane/ethane emission ratio (MER). For example, coal and natural gas emissions are methane-rich (MER = 5–100) with respect to emission ratios measured near oil-storage and oil-processing facilities (MER = 3–5). It is possible that the global-average MER (the ratio of total methane to total ethane emissions from all fossil-fuel sources combined) changed over time as the relative emission strengths of the different fossil-fuel sources varied during the twentieth century.
Fossil fuels

LETTER

Biomass burning and biofuels

The scales of the left and right y-axes show a persistent decline during the 1990s accounts for less than 60% of the total reduction but provide additional evidence that the drop in fossil-fuel emissions started sooner, by about a decade. The decline in fossil-fuel emissions during the 1990s contributed to the decline in methane growth rates. Our results are consistent with such a decline, but provide additional evidence that the drop in fossil-fuel emissions started sooner, by about a decade. The decline in fossil-fuel emissions during the 1990s accounts for less than 60% of the total reduction during 1980–2000 in the two-box model for ethane emissions, which add about 20% to the magnitude of emission reductions calculated above (see Supplementary Information).

It is also possible that the late twentieth century decline in ethane could have been caused by a decrease in the atmospheric lifetime of ethane, but we estimate the likelihood for such changes to be low. Assuming fixed emissions, a 5–6 Tg yr⁻¹ increase in ethane loss (roughly one-third of the peak budget) would be required to account for the observed ethane decline. A change of this magnitude due to increases in OH⁺ concentrations during the late twentieth century is unlikely, but atmospheric levels of chlorine atoms (Cl⁺) might have increased, because of increasing tropospheric NOₓ, increasing tropospheric ozone and increasing acidity of aerosols. A Cl⁺ sink...
of the magnitude required to explain the ethane decline would have a minor effect on the methane budget (−3%), because the relative reactivity of Cl* versus OH* (k_{Cl}/k_{OH}) is considerably smaller for methane than it is for ethane. Accounting for the ethane decline would require an increase of roughly 1.1×10^4 Cl* cm^-3 over the entire marine boundary layer, or a much larger increase if just the polluted boundary layer is considered. Estimates for the clean marine boundary layer are in the range 10^3–10^4 Cl* cm^-3. It is not possible to assess whether a change of the required magnitude is viable with the limited observational data available at present23,25.

**METHODS SUMMARY**

**Firm-air measurements, modelling and inversion.** At all three sites, multiple flasks (see Supplementary Information) from the same depth were filled sequentially, using established methods26,27. All flasks were analysed at the University of California, Irvine, using −100 cm^3 STP samples on a gas chromatography-mass spectrometry (GC-MS) system designed for trace gas analysis on small air samples28. Summit and South Pole flasks were analysed at least twice. We used a one-dimensional firm-air model and a synthesis inversion method to derive atmospheric histories of the annual-mean, high-latitude, tropospheric abundances of ethane from the firm-air measurements (see Supplementary Information).

**Two-box model.** The Northern and Southern hemispheres are represented as equal mass boxes of 2.2×10^10 Tg (exchange time 1 year). Ethane is lost through OH* oxidation (2/3 months^{-1}) and transport into the stratosphere (1/3 yr^{-1}), yielding a present day lifetime of 2.3 months. The annual-mean OH* loss frequency varies over the past 100 years based on the methane feedback on tropospheric OH*: −0.32% in OH* for every +1% in methane29. The OH* changes differently in Northern and Southern hemispheres: −0.305% and −0.335%, respectively, based on simulations with the UCI-CTM11,12. We adopt a methane increase of 900 p.p.b. to 1,790 p.p.b. since 190023. Fossil-fuel, biofuel and biomass-burning sources in the model Northern Hemisphere are adopted from previous work12 and represent 93%, 81% and 58%, respectively, of the total emissions. The fossil-fuel emission histories for various biomass-burning scenarios are developed by an inverse optimization algorithm (see Supplementary Information).

**Three-dimensional model.** The UCI-CTM’s simulation of ethane with realistic distribution of sources10 is used to relate the northern and southern tropospheric mean abundances to the annual-mean abundance over the ice sheets, and thus provide a correction to the two-box model histories for the firn-air modelling.