Large enhancements in southern hemisphere satellite-observed trace gases due to the 2019/2020 Australian wildfires

Richard Pope¹, Brian J Kerridge², Richard Siddans², Barry G Latter², Martyn P Chipperfield¹, Stephen R Arnold¹, Lucy J Ventress², Matilda A Pimlott¹, Ailish M Graham¹, Diane S Knappett², and Richard Rigby¹

¹School of Earth and Environment, University of Leeds, Leeds, United Kingdom ²Remote Sensing Group, STFC Rutherford Appleton Laboratory, Chilton, United Kingdom

November 23, 2022

Abstract

The 2019/2020 Australian wildfires emitted large quantities of atmospheric pollutant gases and aerosols. Using state-of-the-art near-real-time satellite measurements of tropospheric composition, we present an analysis of several emitted trace gases and their long-range transport, and compare to the previous (2018/2019) fire season. Observations of carbon monoxide (CO) show that fire emissions were so intense that the distinct Australian fire plume managed to circumnavigate the Southern Hemisphere (SH) within a few weeks, with eastward propagation over the South Pacific, South America, the South Atlantic, Africa and the Indian Ocean. Elevated atmospheric methane levels were also detected in January 2020 fire plumes over the Pacific, defined using CO as a plume tracer, even though sampling was restricted spatially by aerosols and clouds. Observations also show significant enhancements of methanol from the fires, where CH3OH:CO enhancement ratios increased within the aged plume downwind over the South Pacific indicating secondary in-plume CH3OH formation.

Australian wildfires Richard J. Pope ^{1,2} , Brian J. Kerridge ^{3,4} , Richard Siddans ^{3,4} , Barry G. Latter ^{3,4} , Martyn P. Chipperfield ^{1,2} ,
Richard J. Pope ^{1,2} , Brian J. Kerridge ^{3,4} , Richard Siddans ^{3,4} , Barry G. Latter ^{3,4} , Martyn P. Chipperfield ^{1,2} ,
Stephen R. Arnold ¹ , Lucy J. Ventress ^{3,4} , Matilda A. Pimlott ¹ , Ailish M. Graham ¹ , Diane S. Knappett ^{3,4}
and Richard Rigby ^{1,5}
1: School of Earth and Environment, University of Leeds, Leeds, United Kingdom
2: National Centre for Earth Observation, University of Leeds, Leeds, United Kingdom
3: Remote Sensing Group, STFC Rutherford Appleton Laboratory, Chilton, United Kingdom
4: National Centre for Earth Observation, STFC Rutherford Appleton Laboratory, Chilton, United
Kingdom
5: Centre for Environmental Modelling and Computation, University of Leeds, Leeds, United Kingdom
Submitted to Journal of Geophysical Research: Atmospheres
Key Points
• Satellite-retrieved carbon monoxide (CO) plumes from the Australian fires circumvent the Southern Hemisphere.
 Satellite-retrieved methanol (CH₃OH) shows downwind enhancement of CH₃OH:CO ratio suggesting in-plume secondary CH₃OH production as well as direct emission.
Key Words
Australian Fires; IASI; Carbon Monoxide; Methanol; Methane
Abstract:
The 2019/2020 Australian wildfires emitted large quantities of atmospheric pollutant gases and aerosols. Using state-of-the-art near-real-time satellite measurements of tropospheric composition, we present an analysis of several emitted trace gases and their long-range transport, and compare to the previous (2018/2019) fire season. Observations of carbon monoxide (CO) show that fire

30 Southern Hemisphere (SH) within a few weeks, with eastward propagation over the South Pacific,

- 31 South America, the South Atlantic, Africa and the Indian Ocean. Elevated atmospheric methane
- 32 levels were also detected in January 2020 fire plumes over the Pacific, defined using CO as a plume
- tracer, even though sampling was restricted spatially by aerosols and clouds. Observations also show
- 34 significant enhancements of methanol from the fires, where CH₃OH:CO enhancement ratios
- 35 increased within the aged plume downwind over the South Pacific indicating secondary in-plume
- 36 CH_3OH formation.

37 **1. Introduction**

38 Vegetation fires occur regularly in Australia between the months of August and December (Giglio et 39 al., 2013; van der Werf et al., 2017). Burning activity predominantly occurs in northern Australia, but 40 is widespread across the continent (Andela et al., 2017). Giglio et al., (2013) suggested that the 41 majority of vegetation fires take place on savanna and shrubland, but in south-eastern Australia 42 forest fires are most prevalent (Bradstock et al., 2012; van der Werf et al., 2010). Over recent 43 decades, there have been large-scale decreases in Australian fire activity (Andela et al., 2017; Rabin 44 et al., 2015). However, with present and future climate and land-use change, conditions in Australia 45 are predicted to yield more frequent large-scale fire events (Pitman et al., 2007; Clarke et al., 2011; 46 Di Virgilio et al., 2019). According to the Australian Bureau of Meteorology (2020), the 2019 summer 47 was the warmest (1.52°C above the national average, 1961-1990) and driest (rainfall 40% lower than average) season on record. This provided suitable conditions for wildfires to ignite and spread.

- 48 average) season on record. This provided suitable conditions for wildfires to ignite and spread.
- 49 The Australian wildfires of the 2019/2020 fire season, colloquially known as the "black summer",
- 50 represented some of the largest events in recent decades. The fires burned over 110,000 km² of
- bush, forest and parks (BBC, 2020). The majority of the fire activity occurred in south-eastern
 Australia (New South Wales and Victoria), which is predominantly eucalyptus forest and woodland
- Australia (New South Wales and Victoria), which is predominantly eucalyptus forest and woodland
 (SOTE, 2016). The fires caused 33 deaths (BBC, 2020) and killed over approximately 1 billion animals
- 54 (UoS, 2020). In comparison, the Black Saturday fires (February 2009) in Victoria burned
- 55 approximately 4500 km² and killed 173 people (Siddaway and Petelina, 2011). Though the
- 56 2019/2020 fire death toll was lower, the burned area was much larger producing substantial
- 57 quantities of smoke and pollutants.
- 58 Vegetation fires emit large quantities of smoke/aerosols and trace gases, which have important
- 59 impacts on climate and the atmospheric radiation balance (Li et al., 2017, Rowlinson et al., 2019)
- and surface air quality (AQ, Bowman and Johnston, 2005; Haikerwal et al., 2016; Reisen et al., 2005;
- 61 Kiely et al., 2019). The 2019/2020 Australian fires emitted approximately 250 million tonnes of
- carbon dioxide (CO₂), equivalent to nearly half the country's annual anthropogenic emissions (Hope,
 2020). This combination of fuel type, fire intensity and coverage, yielded large-scale fire plumes
- 64 causing intense local pollution as well as long-range pollution transport. Wildfire-driven pyro-
- convection propagated vertically up into the stratosphere, reaching approximately 30 km (Ohneiser
- 66 et al., 2020) over the South Pacific. In comparison, the Black Saturday fire plume reached 22 km
- 67 (Siddaway and Petelina, 2011).
- 68 In this study, we use state-of-the-art satellite retrievals to provide detailed analysis of the spatial and
- 69 temporal evolution of several trace gas distributions sourced from the 2019/2020 Australian fires.
- 70 While available for the stratosphere, such capabilities were in their infancy when previous major
- 71 burning events occurred in Australia (e.g. February 2009).
- 72
- 73

74 2. Observations

75 2.1 Fire Data Sets

76 We use two different satellite-derived fire activity datasets: fire radiative power (FRP) from the 77 Global Fire Assimilation System (GFAS vn1.2; Kaiser et al., 2012) and burned area (BA) from the Fire 78 INventory from NCAR (FINN near-real-time (NRT) vn1.0; Wiedinmyer et al., 2011). Both products are 79 provided at a daily temporal resolution and are based on direct Moderate Resolution Imaging 80 Spectroradiometer (MODIS) measurements (e.g. FRP and thermal anomalies). These quantities are 81 merged with secondary information (including land surface type and emission factors) to derive topdown emissions for trace gases and aerosols (Kiely et al., 2019; Wooster et al., 2018).

82

83 2.2 Trace Gas Data Sets

84 In this study we use trace gas retrievals from the Infrared Atmospheric Sounding Interferometer 85 (IASI). IASI is a Michelson interferometer which observes the spectral range 645 to 2760 cm^{-1} with spectral sampling of 0.25 cm⁻¹ (Illingworth et al., 2011). It measures simultaneously in four fields of 86 87 view (FOV, each circular at nadir with a diameter of 12 km) which are scanned across track to sample 88 a 2200 km-wide swath (Clerbaux et al., 2009). IASI is one of a suite of nadir-sounders flying on 89 Eumetsat's MetOp-A, -B and -C satellites in sun-synchronous polar orbits with equator crossing times 90 of 9.30 (day) and 21.30 (night). Here we use CO, methanol (CH₃OH) and methane (CH₄) data from 91 MetOp-B produced by NRT processing systems developed by the Rutherford Appleton Laboratory 92 (RAL). CO profiles are co-retrieved with column amounts of CH₃OH, other trace gases and dust in an 93 extended version of RAL's Infrared-Microwave-Sounding (IMS) scheme, which is described in the 94 supplementary material (SM-2). IMS was developed originally to retrieve temperature, water 95 vapour, ozone, surface spectral emissivity and cloud jointly from co-located measurements by IASI, 96 the Microwave Humidity Sounder (MHS) and the Advanced Microwave Sounding Unit (AMSU-A) on 97 MetOp. CH₄ data are retrieved by an improved version of the IASI scheme reported by RAL Space 98 (2015), which is detailed by Siddans et al. (2017). Data are available from the Centre of 99 Environmental Data Analysis (CEDA, Siddans et al., 2020). CO and CH₃OH have been quality filtered 100 for a geometric cloud fraction of 0.5 or less (0.1 or less for CH_4 given the greater sensitivity to 101 interference from cloud/aerosol) and a cost value of 1000.0 or less (120 or less for CH₄ plus a 102 convergence flag equally 1.0). For CO and CH₃OH, we experimented with a stricter geometric cloud 103 fraction threshold of <0.2. We found this had negligible impact on the scientific results, but did 104 reduce the spatial coverage, making the fire signals noisier. Hence we used the <0.5 cloud fraction 105 threshold. We have also investigated more localised enhancements in tropospheric column nitrogen 106 dioxide (TCNO₂) from the Tropospheric Monitoring Instrument (TROPOMI) on-board ESA's Sentinel 5 107 – Precursor (S5P) satellite, which is discussed in the SM (see **SM-1**).

108 3. Results

109 3.1 Fire Activity

110 During the 2019/2020 fire season (November-December-January, NDJ), satellite observations detected substantially larger fire activity on the Australian south-eastern coastline around highly 111 112 populated regions such as Sydney compared to the average of the previous 10 seasons (NDJ 2009-

- 113 2019 climatology). GFAS FRP suggests that on average (NDJ climatology) (Figure 1a) there was
- 114 limited fire activity over south-eastern Australia (i.e. 10-20 mW/m²). The peak activity was more
- widespread across the north-western territories with FRP typically between 20 and 30 mW/m². 115
- 116 However, in NDJ 2019/2020 the entire Australian south-eastern coastline experienced large-scale
- fires with intensities well above 50 mW/m² (Figure 1b). This is supported by the FINN BA (Figure 1c & 117 d) with fire events peaking above 10 km² widespread across the south-east coast. In contrast, the 118

- 119 fire events in the NDJ climatology predominantly occurred over the north-western territories and
- northern coastlines, with lower BA between 3.0 and 7.0 km². Figure 1e shows the time-series of the
- total daily Australian FRP and BA for the climatological (median daily totals, 2009-2019) and
- 122 2019/2020 fire seasons. Between 1st November and 31st January, the climatological FRP has a small
- range (i.e. 25th-75th percentiles) between approximately 0 and 10 GW. Climatological BA ranges
- between approximately near-zero and 1700 km². However, the 2019/2020 FRP (BA) is typically hot ways 20 (100) and 150 (1700) CW ($4\pi^2$) but with peaks in late December (5DD-2220 CW)
- between 20 (100) and 150 (1700) GW (km²), but with peaks in late December (FRP=~320 GW,
 BA=~2200 km²) and early January (FRP=~580 GW, BA=~3000 km²). The peak FRP and BA values sit
- 127 well outside the variability of the climatologies, highlighting the extreme fire activity experienced in
- , 128 the 2019/2020 fire season.

129 **3.2 Carbon Monoxide**

- 130 The 2019/2020 Australian fire season produced extensive quantities of emitted CO, as observed by
- 131 IASI. Figure 2c shows a large total-column CO (TCCO) plume originating over south-eastern Australia 132 and propagating across the entire Pacific, reaching South America. Here, the TCCO ranges between
- approximately $16-21 \times 10^{17}$ molecules/cm², peaking over the Australian coastline and midway
- between continents in the NDJ period 2019/2020. In the previous burning season (NDJ 2018/2019),
- 134 Detween continents in the NDS period 2019/2020. In the previous burning season (NDS 2019/2019), 135 TCCO was considerably lower and ranged between 10-13 $\times 10^{17}$ molecules/cm², with no obvious fire
- 136 signal over Australia (**Figure 2a**). **Figure 2e** shows the difference between fire seasons to be
- 137 widespread and large (1.5-7.5 ×10¹⁷ molecules/cm²) across the Pacific. Peak inter-year differences of
- 138 over 5.0×10^{17} molecules/cm² occur over south-eastern Australia and the mid-Pacific, as the plume
- 139 propagates eastwards. The inter-year differences are significant over large areas (99% confidence
- 140 level based on the student t-test and where absolute mean differences are greater than 1.0×10^{17}
- 141 molecules/cm²) as shown by the green polygon-outlined regions.
- During the 2018/2019 season, fire plumes of limited extent were detected, with moderate CO 142 outflow from the east coast in November 2018 peaking at approximately 19.0 ×10¹⁷ molecules/cm² 143 (Figures 2b & d). In NDJ 2019/2020, there is large and frequent CO outflow throughout the entire 144 season. TCCO peaks at more than 30.0×10^{17} molecules/cm² and persists across the 20°-40°S band. 145 **Figure 2f** shows that the inter-year difference exceeds 15.0×10^{17} molecules/cm² and the larger 146 quantities of CO propagating out into the Pacific (Figure 2c). CO outflow from the peak fire activity 147 (Figure 1e) in late December 2019/early January 2020 went on to circumnavigate the entire SH 148 (Figure 3). Between 27th December 2019 and 9th January 2020, the fire emissions led to large 149 quantities of CO (>25 $\times 10^{17}$ molecules/cm²), which formed large-scale plumes propagating towards 150 South America. Pyroconvection during this period uplifted plumes to altitudes where CO and other 151 trace gases could more easily be detected by IASI (i.e. colder temperatures and above clouds). In the 152 following fortnight, 10th – 23rd January 2020, these plumes reached South America (peak TCCO 153 >20.0×10¹⁷ molecules/cm²) and started propagating into the South Atlantic (15-18×10¹⁷ 154 molecules/cm²). A week later, the TCCO plume reached southern Africa (no local fire sources 155 apparent there, unlike e.g. 15th-28th November 2019) with values still between 15-18×10¹⁷ 156 molecules/cm². The TCCO quantities were also enhanced to 14-16×10¹⁷ molecules/cm² over the 157 Indian Ocean, reaching the Australian west coastline and fully encircling the SH. Over south-eastern 158 159 Australia (black box in Figure S1c), the 2019/2020 fires (NDJ) emitted 9.06 Tg of CO (1.73 times 160 larger than the 2018/2019 annual total anthropogenic Australian CO emissions; NPI, 2020) in 161 comparison to 0.33 Tg in NDJ 2018/2019, based on FINN emissions.
- 162
- 163

164 **3.3. Methanol and Methane**

Focusing on the 3rd – 16th of January 2020, when the fire plumes were most spatially extensive (see 165 TCCO in Figure 3, Figure 4a), CH₃OH and CH₄ both showed substantial increases from the fires 166 (Figures 4b & c). Total column CH₃OH (TCCH₃OH), relative to the 3rd – 16th January 2019, show peak 167 enhancements of over 10×10¹⁵ molecules/cm² co-locating with TCCO enhancements of over 15×10¹⁷ 168 molecules/cm² (Figure 4a). Though CH₃OH infrared absorption features are much weaker than those 169 170 of CO and low background CH₃OH abundances (e.g. over the ocean) are difficult to detect in individual soundings (i.e. large estimated errors; see SM-3, Figure S6), robust signals are detected in 171 large sources such as the Australian fire plume (i.e. >15×10¹⁵ molecules/cm², Figure 5b, SM-3, Figure 172 173 S7).

- 174 CH₄, on spatial and temporal scales observable by satellite fluctuates by only a few % of its global
 175 mean value, unlike the order of magnitude of variability in CO and methanol. To retrieve CH₄
- 176 perturbations at the % level requires careful handling of cloud and, in the case of the Australian
- 177 wildfire plumes, also smoke (and dust). As shown in SM-4 and Figure SM8, IASI detects daily CO
- plumes, but the corresponding CH₄ distribution is less well sampled due to stringent filtering
- 179 necessary for cloud. However, the column average CH₄ (CACH₄) anomaly for the 3rd-16thJanuary
- 180 2020, with reference to the de-trended and de-seasonalised multi-annual mean for January (2007-
- 181 17, MetOp-A & B offline version) (Figure 4c) is positive over much of the region (e.g. ~0.01 ppmv),
- and some features (e.g. 0.015-0.03 ppmv) cohere with prominent structure (e.g. over the central
 South Pacific) in the CO and CH₃OH plumes (see Figure 4a & b). Therefore, we use CO as an in-plume
- 184 tracer to quantify the much lower amplitude CH_4 signals from the fires. **Figure 4d** shows the time
- evolution of in-plume column average CO (CACO) and CACH₄ averaged over 150°E-90°W, 50-20°S
- 186 (black box in **Figure S8**). The in-plume thresholds for CACO and CACH₄were set at 0.07 ppmv and
- 187 1.75 ppmv. Both thresholds had to be met, along with stringent cloud screening and other quality
- 188 control for CH₄, in order for the pair of CO and CH₄ soundings at a given location to be sampled.

189 In the first two weeks of January 2020, the in-plume domain-averaged daily CACO ranges between 190 0.09 and 0.12 ppmv, and the standard deviation indicates large spatial variability. In the second two 191 weeks of January, the spatially-averaged CACO is substantially lower, ranging between 0.07 and 0.08 192 ppmv, with much smaller spatial variability, consistent with mixing with neighbouring CO-poor 193 airmasses in the east and less intense incoming plumes in the west. In contrast, for CACH₄ the 194 spatially averaged value drops only slightly and spatial variability is unchanged in the second two 195 weeks, attributable to mixing with high CH₄ tropical airmasses in the east. The peak average CACH₄values (1.78-1.79 ppmv) occur in the first few weeks and then 27th-29th January. Temporal 196 197 correlation of the spatially averaged CO and CH₄ time series is 0.63 for the whole month and 0.86 198 between 1st and 20th January. The daily spatial correlation in this period is between 0.2 and 0.5, 199 indicative of a substantial fire-induced component of CH₄. In the latter period of January (21st-31st) 200 the correlation drops below 0.0 indicating the fire-induced component to be less significant for CH₄ 201 in comparison to other processes. Overall, the relationship between CO and CH4 in data produced 202 from IASI on MetOp-B demonstrates that the plumes emitted from the Australian fires contained 203 CH₄ as well as CO. Emission factors of CH₄ from vegetation fires have been shown to be similar in 204 magnitude to those of methanol on a mass emitted per mass of dry matter consumed basis (Agaki et 205 al., 2011). It is worth noting that given the long CH₄ lifetime against hydroxyl radical (OH) oxidation 206 (~9 years (McNorton et al., 2016)), any enhancement in methane due to OH suppression in the 207 plume on the transport timescale of a few days would be minimal (~0.1% over 3 days under 208 complete suppression of OH oxidation).

210

211 3.4. Enhancement Ratios

212 We investigate how the TCCH $_3$ OH:TCCO enhancement ratio changes as the fire plume traverses the

- Pacific across the four regional boxes defined in **Figure 5a** between the 1st and 17th January 2020 (i.e.
- period of large fire plume). Box 1 covers the primary fire region and Boxes 2-4 cover the downwind
 outflow. In all cases, we see TCCO-TCCH₃OH correlation values (R in Figure 5c-f) above 0.63, peaking
- at 0.92 in Box 3, indicative of common origins. The in-plume TCCO and TCCH₃OH values are defined
- based on a subjectively chosen threshold (TCCO = 18.0×10^{17} molecules/cm² and TCCH₃OH = 5.0×10^{15}
- 218 molecules/cm² where both criteria have to be met for the two species to be co-sampled), but
- sensitivity analysis of these thresholds (**Figure SM5, Table S1**), and the time period in which the

220 plume(s) are sampled, show that our results are robust and relatively insensitive to our choices of

- these parameters.
- In Box 1, the TCCH₃OH:TCCO enhancement ratio (M), based on a simple linear least-squares fit, is
- 223 0.0036 \pm 5.98%, which is similar to the FINN CH₃OH:CO fire emissions ratio (0.0031 \pm 0.04%). This
- suggests that the satellite observations of atmospheric enhancements close to the fires are
- 225 consistent with freshly emitted fire pollution. As the plume propagates eastwards over the Pacific,
- there is an increase in the TCCH₃OH:TCCO enhancement ratio. In Boxes 2, 3 and 4 M is
- 227 0.0059±3.13%, 0.0091±1.28% and 0.0081±1.94%, respectively. When using the full range of the IASI
- TCCH₃OH retrievals (i.e. the retrieval values \pm the random errors) and recalculating the enhancement ratios, we find that M is perturbed by approximately 10%, which is relatively small, and the regional
- ratios follow the same tendency. This increase of TCCH₃OH with distance, and therefore time, from
- the fires is suggestive of in-plume chemical production of CH₃OH. This is similar to Holzinger et al.,
- 232 (2005) and Coheur et al., (2009), who used aircraft and satellite data respectively, to investigate fire
- plume $CH_3OH:CO$ enhancement ratios suggesting signs of secondary CH_3OH production when
- studying southern European fire plumes. The magnitude of the CH₃OH/CO enhancement ratios
 derived here are consistent with other studies (e.g. Yokelson et al., 1999; Christian et al., 2003;
- Holzinger et al., 2004; Singh et al., 2004; Karl et al., 2007). Our results imply that IASI detected such
- 237 secondary formation of CH₃OH within the fire plume, but with a robust enhancement across the
- large portion of the Pacific, on a scale previously not discussed in the literature, to the best of our
 knowledge. Mixing with background air would likely dilute the plume counteracting some of the
- downwind increase in CH_3OH enhancement relative to CO. This suggests that the in-plume
- production of CH_3OH is likely larger than that suggested by the observed increase in the CH_3OH :CO
- ratio alone. Such large-scale enhancements in CH₃OH may have an important influence on the
- 243 CH₃OH budget, impact the oxidative capacity of the remote atmosphere, and potentially the CH₄
- 244 lifetime (Read et al., 2012). Such secondary methanol production could be driven by the self-
- reaction of methylperoxy (CH_3O_2), the reaction of CH_3O_2 with higher order peroxy (RO_2) radicals
- 246 (Jacob et al., 2005) and OH (Müller et al., 2016), or possibly by less well-established oxidation of
- 247 organics in the fire plume (Holzinger et al., 2005).

248 **4.** Conclusions

249 The 2019/2020 Australian fires ("black summer") constituted some of the largest regional wildfires

- in recent decades and produced large quantities of smoke, aerosols and trace gases. Peak fire
- activity occurred on eucalyptus forest vegetation in south-eastern Australia during December and
- 252 January. Data from the MetOp-B satellite produced by RAL's NRT processing system show that
- carbon monoxide (CO) emitted from the fires circumnavigated the entire Southern Hemisphere.
- 254 Compared with the 2018/2019 fire season, CO levels from the fire-plumes were substantially (and

- significantly, 99% confidence level) larger by approximately 30-70% over the South Pacific in the
 November-December-January average.
- 257 Methanol (CH₃OH), which is difficult to detect in normal circumstances due to its weak absorption
- 258 signature, was in sufficient abundance to retrieve in-plume column amounts with a good precision.
- 259 Satellite-observed enhancements in total column CH₃OH relative total column CO show a substantial
- increase downwind from the fires, over the Pacific Ocean. This is strongly suggestive of CH₃OH
- 261 production within the plume, on a scale not previously reported, as far as we are aware, with
- 262 potentially important implications for the methanol budget and oxidative capacity of the remote
- atmosphere. Elevated levels of CH₄ were also detected in association with the fire-plumes during
- peak activity in early-mid January 2020, even though the CH₄ emission rate is considerably lower
- than for CO and perturbations from uniform mixing less than 2%.
- 266 With future climate and land-use change it is expected that wildfires are going to become more
- 267 frequent and intense. Therefore, Earth observation (EO), as presented here, is going to be a vital
- resource to help monitor and understand future wildfire events globally. These EO capabilities will
- 269 improve with the planned launches of advanced infrared and shortwave spectrometers such as IASI
- 270 Next Generation and Sentinel 5 on the MetOp Second Generation in polar orbit (ESA, 2020) and the
- 271 Infrared Sounder and Sentinel 4 on Meteosat Third Generation in geostationary orbit.

272 Acknowledgements

- 273 This work was supported by the UK Natural Environment Research Council (NERC) by providing
- 274 funding for the National Centre for Earth Observation (NCEO, award reference NE/R016518/1).
- 275 TROPOMI tropospheric column NO₂ data came from KNMI, which is available at
- 276 <u>http://www.temis.nl/airpollution/no2.html</u>. FINN NRT vn1.5 burned area and GFAS FRP data came
- 277 from NCAR (https://www.acom.ucar.edu/acresp/forecast/fire-emissions.shtml) and ECMWF-CAMS
- 278 (https://apps.ecmwf.int/datasets/data/cams-gfas/). Meteorological reanalysis data was obtained
- 279 from NCEP (<u>https://psl.noaa.gov/data/gridded/data.ncep.reanalysis.html</u>). RAL's NRT system
- 280 processes Eumetsat Level-1 data from MetOp-B IASI, MHS, AMSU and GOME-2 and uses ECMWF
- 281 meteorological forecast data, all processed on RAL's Jasmin infrastructure. We will upload the data
- to the UK Centre for Environmental Data Analysis (CEDA) archive upon acceptance. For the purposes
- of review, our data is available at <u>http://homepages.see.leeds.ac.uk/~earrjpo/iasi_data/.</u>

284 References

- Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and
- 286 Wennberg, P. O. (2011). Emission factors for open and domestic biomass burning for use in
- 287 atmospheric models. *Atmos. Chem. Phys.* **11**, 4039–72, <u>https://doi.org/10.5194/acp-11-4039-2011</u>.
- 288
- Andela, N., Morton, D. C., Giglio, L., Chen, Y., van der Werf, G. R., Kasibhatla, P. S., et al. (2017). A
- human-driven decline in global burned area. *Science* **356**, 1356-1362. DOI: 10.1126/science.aal4108.
- 291
- Australian Bureau of Meteorology. (2020). Annual climate statement 2019.
- 293 http://www.bom.gov.au/climate/current/annual/aus (last accessed 17/08/2020).
- 294
- 295 BBC. 2020. Australia fires: A visual guide to the bushfire crisis. https://www.bbc.co.uk/news/world-
- australia-50951043 (last accessed 17/08/2020).
- 297

- Bowman, M. J. S and Johnston, F. H. 2005. Wildfire Smoke, Fire Management, and Human Health.
- 299 *EcoHealth* **2**, 76-80. doi: 10.1007/s10393-004-0149-8.
- 300

Bradstock, R. A., Cary, G. J., Davies, I., Lindenmayer, B. D., Price, O. F. and Williams, R. J. 2012.

302 Wildfires, fuel treatment and risk mitigation in Australian eucalypt forests: Insights from landscape-

- scale simulation. *Journal of Environmental Management* **105**, 66-75.
- 304 doi.org/10.1016/j.jenvman.2012.03.050.
- 305

Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Saharjo, B. H. and
Ward, D. E. 2003. Comprehensive laboratory measurements of biomass-burning emissions: 1.
Emissions from Indonesian, African, and other fuels. *Journal of Geophysical Research - Atmospheres* **108**, 4719, doi:10.1029/2003JD003704.

310

Clarke, H. G., Smith, P. L. and Pitman, A. J. 2010. Regional signatures of future fire weather over
eastern Australia from global climate models. International Journal of *Wildland Fire* 20 (4), 550-562.
doi.org/10.1071/WF10070.

314

Clerbaux, C., Boynard, A., Clarisse, L., George, M., Hadji-Lazaro, J., Herbin, H., Hurtmans, D.,

Pommier, M., Razavi, A., Turquety, S., Wespes, C. and Coheur, F-P. 2009. Monitoring of atmospheric
composition using the thermal infrared IASI/MetOp sounder. *Atmospheric Chemistry and Physics* 9,
6041-6054. doi.org/10.5194/acp-9-6041-2009.

319

Coheur, P-F., Clarisse, L., Turquety, S., Hurtmas, D. and Clerbaux, C. 2009. IASI measurements of
 reactive trace species in biomass burning plumes. *Atmospheric Chemistry and Physics* 9, 5655-5667.
 doi.org/10.5194/acp-9-5655-2009.

323

Di Virgilio, G., Evans, J. P., Blake, S. A. P., Armstrong, M., Dowdy, A. J., Sharples, J., and McRae,
R. 2019. Climate change increases the potential for extreme wildfires. *Geophysical Research Letters* 46, 8517–8526. doi.org/10.1029/2019GL083699.

327

328 ESA. 2020. Sentinel Overview. https://sentinel.esa.int/web/sentinel/missions (last accessed
329 17/08/2020).

330

331 Giglio, L., Randerson, J. T. and van der Werf, G. R. 2013. Analysis of daily, monthly, and annual

- burned area using the fourth-generation global fire emissions dataset (GFED4). *Journal of Geophysical Research: Biogeosciences* 118, 317-328. doi:10.1002/jgrg.20042.
- 334

338

Haikerwal, A., Akram, M., Sim, M. R., Meyer, M., Abramson, M. J. and Dennekamp, M. 2016. Fine
particulate matter (PM_{2.5}) exposure during a prolonged wildfire period and emergency department
visits for asthma. *Respirology* 21, 88-94. doi:10.1111/resp.12613.

- Holzinger, R., Williams, J., Salisbury, G., Klüpfel, T., de Reus, M., Traub, M., Crutzen, P. J. and
- Lelieveld, J. 2005. Oxygenated compounds in aged biomass burning plumes over the East
- 341 Mediterranean: evidence of strong secondary production of methanol and acetone. *Atmospheric*
- 342 *Chemistry and Physics* **5**, 39-46. doi.org/10.5194/acp-5-39-2005.

343							
344	Hope, M. 2020. Australian Burning. The Lancet Planetary Health 4 (1), E12-E13.						
345	dio.org/10.1016/S2542-5196(20)30006-1.						
346							
347	Illingworth, S. M., Remedios, J.J., Boesch, H., Moore, D. P., Sembhi, H., Dudhia, A. and Walker, J. C.						
348	2011. ULIRS, an optimal estimation retrieval scheme for carbon monoxide using IASI spectral						
349	radiances: sensitivity analysis, error budget and simulations. Atmospheric Measurement Techniques						
350	4 , 269-288. doi:10.5194/amt-4-269-2011.						
351							
352	Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh,						
353	H. B. and Guenther, A. 2005, Global budget of methanol: Constraints from atmospheric						
354	observations, Journal of Geophysical Research 110, D08303, doi:10.1029/2004JD005172.						
355							
356	Kaiser, J. W., Hell, A., Andreae, M. O., Benedetti, A., Chubarova, N., Jones, L., et al. (2012). Biomass						
357	burning emissions estimated with a global fire assimilation system based on observed fire radiative						
358	power. <i>Biogeosciences</i> 9 , 527-554. https://doi.org/10.5194/bg-9-527-2012.						
359							
360	Karl, T. G., Christian, T. J., Yokelson, R. J., Artaxo, P., Hao W. M. and Guenther, A. 2007. The Tropical						
361	Forest and Fire Emissions Experiment: method evaluation of volatile organic compound emissions						
362	measured by PTR- MS, FTIR, and GC from tropical biomass burning. Atmospheric Chemistry and						
363	<i>Physics</i> 7 (22), pp.5883-5897.						
264							
265	Kiely I Spracklen D. V. Wiedinmver C. Conihear I. Beddington C. I. Archer-Nicholls S. Lowe D.						
366	Arnold S.A. Knote C. Khan M.F. Latif M.T. Kuwata M. Budisulistiorini S.H. and Svaufina J.						
367	2010 New estimate of particulate emissions from Indonesian peat fires in 2015 Atmospheric						
368	Chemistry and Physics 19 11105-11121 doi org/10 5194/acp-19-11105-2019						
360	chemistry and r hysics 13, 11105-11121, doi.org/10.5154/acp-15-11105-2015.						
370	Li F. Lawrence, D. M. and Bond-Lamberty, B. 2017. Impact of global land surface air temperature						
370	and energy hudget for the 20 th Century due to changes within ecosystems. <i>Environmental Research</i>						
372	Letters 12 04/014 doi org/10 1088/1748-9326/aa6685						
372	Letters 12, 044014. doi.org/10.1000/1740 5520/dd0005.						
374	McNorton I Chinnerfield M P. Gloor M. Wilson C. Feng W. Hayman G. D. Rigby M						
374	Krummel P B O'Doberty S Prinn R G Weiss R F Young D Dlugokencky F and Montzka S						
376	A (2016) Role of OH variability in the stalling of the global atmospheric CH4 growth rate from 1999						
277	to 2006. Atmos Cham Phys 16 , 7042–7056. https://doi.org/10.5104/2cp16-7042-2016						
270	to 2000. Atmos. Chem. Phys. 10, 7945-7950, https://doi.org/10.5194/acp10-7945-2010.						
370	Müller LE Liu 7 Nauven V S Stavrakou T Harvey I N and Peeters I 2016 The reaction of						
380	methyl perovy and hydroxyl radicals as a major source of atmospheric methanol. <i>Nature</i>						
201	Communications 7 12212 doi:10.1029/ncomms12212						
201							
202 202	NRL 2020 National Bollutant Inventory, http://www.ppi.gov.au/ppidata/action/load/browso						
201	search/criteria/browse_type/Location/year/2010/lact accessed 17/08/2020						
204	3 can chromatic harmonic bio wise-typer location ryear 2013 (last accessed 17/00/2020).						
202	Obneiser K. Ansmann A. Baars H. Seifert D. Baria P. Jimanoz C. Padenz M. Teisseire A						
200 207	Children R., Anstriann, A., Dadis, H., Senert, F., Ddijd, D., Jintenez, C., Rauenz, IVI., reissene, A.,						
20/ 200	Mandering 11, 2020. Smalle of extreme Australian hyphilizes cheened in the strateschere ever Durite						
200	wandering, O. 2020. Smoke of extreme Australian businnes observed in the stratosphere over Punta						

- 389 Arenas, Chile, in January 2020: optical thickness, lidar ratios, and depolarization ratios at 355 and 390 532 nm. Atmospheric Chemistry and Physics **20**, 8003-8015, doi.org/10.5194/acp-20-8003-2020. 391 392 Pitman, A. J., Narisma, G.T. and McAneney, J. 2007. The impact of climate change on the risk of 393 forest and grassland fires in Australia. Climatic Change 84, 383-401. doi:10.1007/s10584-007-9243-6. 394 395 Rabin, S. S., Magi, B. I., Shevliakova, E. and Pacala, S. W. 2015. Quantifying regional, time-varying 396 effects of cropland and pasture on vegetation fire. Biogeosciences 12, 6591-6604. 397 doi.org/10.5194/bg-12-6591-2015. 398 399 RAL Space. 2015. Optimal Estimation Method retrievals with IASI, AMSU and MHS – Final Report 400 Version 5.2. http://cedadocs.ceda.ac.uk/1377/1/iasi_mhs_final_report_v5p2.pdf (last accessed 401 17/08/2020). 402 403 Read, K. A., Carpenter, L. J., Arnold, S. R., Beale, R., Nightingale, P. D., Hopkins, J. R., Lewis, A. C., Lee, 404 J. D., Mendes, L. and Pickering, S. J. 2012. Multiannual observations of acetone, methanol, 405 acetaldehyde in remote tropical Atlantic air: Implications for atmospheric OVOC budgets and 406 oxidative capacity, Environmental Science Technology 46, 20, 11028-11039, doi:10.1021/es302082p. 407 Reisen, F., Meyer, C. P., McCaw, L., Powell, J. C., Tolhurst, K., Keywood, M. D. and Gras, J. L. 2005. 408 Impact of smoke from biomass burning on air quality in rural communities in southern Australia. 409 Atmospheric Environment 45 (24), 3944-3953. doi.org/10.1016/j.atmosenv.2011.04.060. 410 411 Rowlinson, M, J., Rap, A., Arnold, S. R., Pope, R. J., Chipperfield, M. P., McNorton, J., Forster, P., 412 Gordon, H., Pringle, K. J., Feng, W., Kerridge, B. J., Latter, B. L. and Siddans, R. 2019. Impact of El 413 Niño–Southern Oscillation on the interannual variability of methane and tropospheric ozone. 414 Atmospheric Chemistry and Physics 19, 8669-8686. doi.org/10.5194/acp-19-8669-2019. 415 416 Siddans, R., Knappett, D., Kerridge, B.J, Waterfall, A., Hurley, J., Latter, B., Boesch, H. and Parker, R. 417 2017. Global height-resolved methane retrievals from the Infrared Atmospheric Sounding 418 Interferometer (IASI) on MetOp, Atmospheric Measurement Techniques 10, 4135-4164, doi: 419 10.5194/amt-10-4135-2017. 420 Siddans, R. Knappett, D., Kerridge, B., Latter, B. and Waterfall, A. 2020. STFC RAL methane retrievals 421 from IASI on board MetOp-A, version 2.0. Centre for Environmental Data Analysis, 10 March 2020. 422 doi:10.5285/f717a8ea622f495397f4e76f777349d1. 423 424 Siddaway, J. M. and Petelina, S. V. 2011. Transport and evolution of the 2009 Australian Black 425 Saturday bushfire smoke in the lower stratosphere observed by OSIRIS on Odin. Journal of 426 *Geophysical Research* **116**, D06203. doi:10.1029/2010JD015162. 427 428 Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, 429 D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S. and 430 Fuelberg, H. 2004. Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile 431 organic chemicals based on measurements over the Pacific during TRACE-P. Journal of Geophysical 432 *Research* **109**, D15307, doi:10.1029/2003JD003883. 433
 - 10

434 SOTE. 2016. Vegetation Land (2016).

- 435 https://soe.environment.gov.au/theme/land/topic/2016/vegetation-0 (last accessed 17/08/2020).
 436
- 437 UoS. 2020. More than one billion animals killed in Australian bushfires.
- https://www.sydney.edu.au/news-opinion/news/2020/01/08/australian-bushfires-more-than-onebillion-animals-impacted.html (last accessed 17/08/2020).
- 440
- 441 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., Morton, D. C., DeFries,
- 442 R. S., Jin, Y. and van Leeuwen, T. T. 2010. Global fires emissions and the contributions from

deforestation, savannah, forest, agricultural and peat fires (1997-2009). *Atmospheric Chemistry and Physics* 10, 11707-11735. doi:10.5194/acp-10-11707-2010.

- van der Werf, G. R., Randerson, J. T., Giglio, L., van Leeuwen, T. T., Chen, Y., Rogers, B, M., et al.
 2017. Global fire emission estimates during 1997-2016. *Earth System Science Data* 9, 697-720.
- 448 https://doi.org/10.5194/essd-9-697-2017.
- 449

445

- 450 Wiedinmyer, C., Akagi, S. K., Yokelson, R. J., Emmons, L. K., Al-Saadi, A. J., Orlando, J. J. and Soja, A. J.
- 451 2011. The Fire INventory from NCAR (FINN): a high resolution global model to estimate the
- 452 emissions from open burning. *Geoscientific Model Development* 4, 624-641. doi.org/10.5194/gmd-4-453 625-2011.
- 454
- Wooster, M. J., Gaveau, D, L, A., Salim, M. A., Zhang, T., Xu, W., Green, D. C., et al. (2018). New
 Tropical Peatland Gas and Particulate Emissions Factors Indicate 2015 Indonesian Fires Release Far
- 457 More Particulate Matter (but Less Methane) than Current Inventories Imply. *Remote Sensing* **10**(4), 458 495. https://doi.org/10.3390/rs10040495.
- 459
- 460 Yokelson, R. J., Goode, J. G., Ward, D. E., Susott, R. A., Babbitt, R. E., Wade, D. D., Bertschi, I., Griffith,
- D. W. T. and Hao, W. M. 1999. Emissions of formaldehyde, acetic acid, methanol, and other trace
 gases from biomass fires in North Carolina measured by airborne Fourier transform infrared
- 463 spectroscopy. *Journal of Geophysical Research* **104**, 30109–30125.

464

466 Figures



467

468 **Figure 1:** Global Fire Assimilation (GFAS) fire radiative power (FRP, mW/m²) for a) November-

469 December-January (NDJ) climatology (2009-2019) and b) NDJ 2019/2020. Panels c) and d) show Fire

470 INventory from NCAR (FINN) burned area (km²) for c) NDJ climatology and d) NDJ 2019/2020. Panel

e) shows daily time series of accumulated FRP (GW, blue solid line) and BA (km², red line) across

472 Australian for NDJ 2019/2020. The orange and light blue shading represent the 25th-75th percentile

473 spread in the climatology for FRP and BA, respectively.





476 **Figure 2:** Infrared Atmospheric Sounding Interferometer (IASI) NDJ total-column carbon monoxide

477 (TCCO, 10¹⁷molecules/cm²) for a) 2018/2019, c) 2019/2020 and e) 2019/2020-2018/2019 difference.

478 Green polygon-outlined regions in panel e) represent statistically significant differences between the

479 fire seasons at the 99% confidence level (CL, based on the Student t-Test) and where absolute

480 differences are greater than 1.0×10¹⁷ molecules/cm². Panels b), d) and f) represent Hovmöller

481 diagrams of IASI TCCO from November – January at 155°E, between 70°S-0°S (white dashed line in

482 panel a)), for 2018/2019, 2019/2020 and 2019/2020-2018/2019 difference, respectively.



484 **Figure 3:** Temporal evolution of the IASI mean TCCO (10¹⁷molecules/cm²) between the 15th

485 November 2019 and 13th February 2020. Each panel represents a 2-week average with a weekly step

486 between the first day of each map. The arrows show 500 hPa winds from the National Centers for

487 Environmental Prediction (NCEP) reanalysis.

488





Figure 4: a) IASI two-week (3rd-16th January) 2020 - 2019 difference a) TCCO (10¹⁷molecules/cm²) 490 and b) total column methanol (TCCH₃OH, 10¹⁵molecules/cm²). Grey regions represent missing 491 492 satellite data (i.e. average values with error terms >15.0×10¹⁵ molecules/cm²). c) Two-week (3rd-16th January 2020) column average methane (CH₄, ppmv) anomaly with respect to the de-seasonalised 493 and de-trended multi-annual mean for January (2007-2017). d) Daily time series of spatially 494 averaged in-plume (150°E-90°W, 50-20°S; black box in Figure S4) IASI-observed CO (red) and CH₄ 495 496 (blue) column average mixing ratios for January 2020. In-plume data are defined where CO and CH₄ 497 values are both larger than the corresponding thresholds of 0.07 ppmv and 1.75 ppmv. Dashed lines

represent the uncertainty range (average ± standard deviation). The black line represents daily
 spatial correlations between in-plume CO and CH₄. R_all, R_1-20 and R_21-31 are the CO-CH₄ time

500 series correlations for all of January, 1st-20th January and 21st-31st January, respectively.





503 **Figure 5**: a) TCCO and b) TCCH₃OH (10¹⁷ molecules/cm²) for 1st-17th January 2020. White regions

504 represent missing satellite data (i.e. average values with error terms >15.0×10¹⁵ molecules/cm²).

505 Panels c) – f) show scatter plots of TCCH $_3$ OH versus TCCO within Boxes 1-4 outlined in panel a) with

values of correlation (R) and gradient (enhancement ratio, M) indicated.

1 Supplementary Material for "Large enhancements in southern hemisphere satellite-observed

2

trace gases due to the 2019/2020 Australian wildfires"

3 Richard J. Pope^{1,2}, Brian J. Kerridge^{3,4}, Richard Siddans^{3,4}, Barry G. Latter^{3,4}, Martyn P. Chipperfield^{1,2},

4 Stephen R. Arnold¹, Lucy J. Ventress^{3,4}, Matilda A. Pimlott¹, Ailish M. Graham¹, Diane S. Knappett^{3,4}

5 and Richard Rigby^{1,5}

6 Supplementary Material (SM)-1: Satellite Observed Nitrogen Dioxide (NO₂)

7 We use tropospheric column NO₂ (TCNO₂) data from the TROPOspheric Monitoring Instrument

8 (TROPOMI) on-board the ESA's Sentinel-5 Precursor (S5P) satellite (Veefkind et al., 2012). S5P was

9 launched in October 2017 into a sun-synchronous polar orbit with a local overpass time of

10 approximately 13.30. TROPOMI is a nadir-viewing instrument with spectral ranges of 270-500 nm

11 (UV-Vis), 675-775 nm (near-infrared, NIR) and 2305-2385 nm (shortwave-infrared, SWIR). The

12 TROPOMI retrievals represent the highest resolution of any current tropospheric trace gases sensor

13 with a nadir horizontal resolution of 3.5 km × 7.0 km in the UV-Vis-NIR and 7.0 km × 7.0 km in the

14 SWIR.

15 The response of TCNO₂ to the NDJ 2019/2020 Australian fires is less pronounced relative to the

16 other trace gases investigated here due to the relatively short NO₂ lifetime of a few hours (Logan

17 1983; Alvarado et al., 2010). In December 2018 (**Figure S1a**), there are clear TCNO₂ hotspots (0.5-1.5

 $\times 10^{15}$ molecules/cm²) in the north-western territories which clearly overlap with GFAS FRP (**Figure 1a**

19 of the main manuscript). Similar relationships are seen near the coast in Queensland. Clear urban

signals exist such as Sydney (over 4.0×10^{15} molecules/cm²), Melbourne (over 4.0×10^{15}

21 molecules/cm²) and Brisbane/Adelaide (1.0-2.0 ×10¹⁵ molecules/cm²). However, in December 2019

(Figure S1b), there was a large spatial increase in TCNO₂ values > 4.0×10^{15} molecules/cm² around

23 Sydney. Again, these TCNO₂ hotspots are spatially correlated with fire activity (**Figure 1**) suggesting

24 that fires have degraded the air quality in urban regions. Figure S1c shows the difference between

25 December 2019 and 2018, where there are mixed TCNO₂ differences across the northern states,

26 with enhancements $(0.0-1.0 \times 10^{15} \text{ molecules/cm}^2)$ in the Western Australia territory and along the

south-eastern coastline $(2.0 \times 10^{15} \text{ molecules/cm}^2)$. To rule out other sources (e.g. urban) driving the

28 TCNO₂ enhancement along the south-eastern coastline, TCNO₂ values have been weighted by FRP

29 over the region (black box, **Figure S1c**) for the 2018/2019 (**Figure S1d**, red line) and 2019/2020

30 (Figure S1d, blue line). The FRP-weighted TCNO₂ signal for both seasons highlights sizeable

31 variability, but 2019/2020 TCNO₂ values are larger in the first 20 days of November $(3.0-6.0 \times 10^{15})$

32 molecules/cm²), peak in early December (>7.5 ×10¹⁵ molecules/cm²) and remain larger for most of

33 December. Overall, the time period average 2018/2019 and 2019/2020 FRP-weighted TCNO₂ values

34 are approximately 2.2×10^{15} molecules/cm² and 3.3×10^{15} molecules/cm², respectively. To reduce the

35 likelihood of this fire-TCNO₂ signal being dominated by other sources, **Figure S1e** shows time-series

36 where the 2019/2020 TCNO₂ has been weighted by the 2018/2019 FRP and the 2018/2019 TCNO₂

has been weighted by the 2019/2020 FRP. The 2018/2019 TCNO₂ time-series (red lines in Figures

S1d & e) are generally similar suggesting the NO₂ signal is not overly dependent on fire activity.

However, in the 2019/2020 season (blue lines in **Figure S1e & d**), the time-series are substantially

40 different where the 2019/2020 TCNO₂ series weighted by the 2018/2019 FRP is lower (0-3 $\times 10^{15}$

41 molecules/cm²). Therefore, the large 2019/2020 TCNO₂ values are highly likely to be driven primarily

42 by fire activity along the south-east coastline, especially around Sydney.

43 SM-2: Infrared and Microwave Sounding Extended Scheme

- 44 The original Infrared and Microwave Sounding (IMS) scheme was developed to retrieve water
- 45 vapour, temperature and stratospheric ozone profiles from the Infrared Atmospheric Sounding
- 46 Interferometer (IASI), Microwave Humidity Sounder (MHS) and Advanced Microwave Sounding Unit
- 47 (AMSU) on the MetOp-A satellite (Siddans et al., 2015). This was used to produce a Version 1 data
- 48 set from the MetOp-A mission 2007-16 (Siddans et al., 2018), which was delivered to the ESA
- 49 Climate Change Initiative (<u>http://cci.esa.int/watervapour</u>).

50 The IMS scheme uses RTTOV as the radiative transfer model (forward model, FM). The optimal

- 51 estimation method (OEM) is used to infer the atmosphere / surface state which best matches the
- 52 observations, taking into account prior knowledge of the state. This is achieved by minimising the
- 53 cost function:

$$\chi^{2} = (y - F(x))^{T} S_{y}^{-1} (y - F(x)) + (a - x)^{T} S_{a}^{-1} (a - x)$$

54

83

55 y is a vector containing each measurement used by the retrieval (a subset of all the channels 56 available); S_{y} is a covariance matrix describing the errors on the measurements; F(x) represents the FM (RTTOV); S_a is the *a priori* error covariance matrix, which describes the assumed errors on 57 58 the *a priori* estimate of the state, *a*. The solution state which minimises the cost function is found 59 via the Levenberg Marquardt approach (Rodgers, 2000), using the weighting function matrix, K. This 60 contains the derivatives of the measurements with respect to each element in the state vector 61 (evaluated by the FM at a particular estimate of the state). 62 The IMS scheme has now been extended to retrieve tropospheric ozone, CO profiles and column 63 amounts of additional trace gases, dust and volcanic sulphuric acid aerosol. Retrieval of those

64 constituents benefit from accurate, co-located temperature, humidity and spectral emissivity which 65 are co-retrieved by the IMS extended scheme. The IMS extension builds on new capabilities of 66 RTTOV12 to model atmospheric scattering. Cloud and aerosol are modelled as scattering layers and 67 each are retrieved in terms of an optical depth and layer height. Spectral absorption features of 68 methanol, ammonia, formic acid, sulphur dioxide and nitric acid are optically thin. Therefore, these 69 gases are retrieved by adopting a fixed reference profile shape for each and including in the state 70 vector a scale factor for that profile with an extremely large *a priori* uncertainty. The reference 71 profile for each gas is a constant i.e. height independent volume mixing ratio of 1 ppbv. The 72 retrieved scale factors correspond, therefore, to column-averaged mixing ratios in ppbv which would

73 pertain if the assumed flat profile shape was correct.

74 Most variables in the IMS extended state vector can be modelled directly by RTTOV12 (temperature, 75 water vapour, ozone and carbon monoxide profiles, surface spectral emissivity and mass mixing ratio 76 profiles of aerosol components). RTTOV12 can simulate variations in these quantities and returns 77 the weighting functions needed for their optimal estimation. Although RTTOV12 does not explicitly 78 model other minor gases, including methanol, it can compute the derivatives of simulated spectral 79 radiances with respect to changes in the total absorption coefficient profile. Since their absorption 80 features are optically thin, the radiance perturbation due to each gas can be calculated and added to 81 the directly calculated RTTOV12 radiance as follows:

82
$$R'(x) = R(x) + x_{gas} \sum_{i=1}^{N} \frac{dR(x)}{dk_i} C_{gas} n_i$$

Equation 2

Equation 1

- 84 Where R(x) is the RTTOV12 model simulation excluding minor gases. For a given gas in layer i of the
- 85 N (=101) layers in the RTTOV12 model atmosphere, k_i is the (total) volume absorption coefficient
- (cm⁻¹), C_{gas} is the absorption cross section (cm²); n_i is the number density (molecules cm⁻³) at level i 86
- 87 and x_{gas} is the scale factor for the gas (as included in state vector x). Vertical sensitivity (e.g.
- 88 air/surface temperature contrast, presence of cloud, optical thickness of other gases) is accounted
- for through the modelling of $\frac{dR(x)}{dk_i}$ by RTTOV12. 89

90 In total 119 IASI channels are used. Channels selected in the CO and methanol spectral ranges are 91 indicated in Figure S2a and b. The measurement error covariance for IASI is assumed to be diagonal

- 92 with variances as defined in the L1 file.
- 93 CO vertical profiles are retrieved in the extended IMS scheme in an analogous way to temperature,
- 94 water vapour and ozone profiles in the original IMS scheme. Profiles are defined by the retrieval
- 95 state vector (see below) on the 101 pressure levels on which the RTTOV12 coefficients for IASI are
- 96 given. Surface temperature and surface emissivity are also defined by the state vector. Values for 2m
- 97 temperature and 2m water vapour (also input parameters to RTTOV12) are defined by interpolating
- 98 the profiles defined by the state vector. Surface pressure is defined from European Centre for
- 99 Medium-Range Weather Forecasting (ECMWF) analysis (ERA-Interim), adjusted to the mean altitude
- 100 within the IASI footprint assuming the logarithm of the surface pressure varies linearly with the
- 101 difference between the IASI altitude and that of the ECMWF model. This is the only parameter
- 102 defined directly from NWP data in the IMS version 1 data.
- 103 The IMS state-vector x is defined such that there are no correlations between different retrieved 104 product so corresponding off-diagonal elements in the prior covariance matrix are all zero.

105 Temperature (including surface temperature), water vapour, ozone and CO profiles are internally 106 represented using basis functions, $\mathbf{M}_{\mathbf{x}}$, which are the Eigenvectors of a covariance matrix which 107 represents the prior variability of the profile on the 101 RTTOV pressure levels. 28 vectors are fitted 108 for water vapour, 18 for water vapour, 10 for ozone and CO. Covariance matrices were computed 109 using analyses for the three days 17 April, 17 July, 17 October 2013 from ECMWF for temperature and water vapour and the Copernicus Atmosphere Monitoring Service (CAMS) for ozone and CO. The 110 111 zonal mean over all three days was computed and the covariance matrix used to define the state 112 vector was calculated from the differences between all the individual profiles and their zonal mean. Global variability in CO during those days included that due to wild fires, the eigenvectors are 113 therefore capable of representing plumes from such sources. The zonal mean and covariances were 114

- 115 computed in K for temperature and ln(vmr) for water vapour, ozone and CO. The state vector
- comprises the coefficients of the Eigenvectors of the covariance matrix. Temperature profiles in (K) 116 117 on the 101 RTTOV pressure levels are defined from the corresponding 28 elements of the state
- 118 vector as follows:

$T = m_T(\lambda) + M_T x_T$ 119

120

- Equation 3 121 Where m_T is the zonal mean (interpolated to the latitude of observation); M_T is the matrix of
- 122 Eigenvectors and x_T the temperature sub-set of the state vector.
- 123 Water vapour, ozone profiles and CO (in ppmv) are defined similarly (now with exponent):
- $w = e^{m_W(\lambda) + M_W x_W}$ 124

125

Equation 4

- 126 In terms of the state vector representation used in the OEM, the *a priori* state vector elements for
- 127 temperature, water vapour, ozone and CO are all zero (the zonal mean profile is added in the FM).
- 128 The prior covariance is diagonal with variances given by the Eigenvalues of the covariance matrix.
- 129 In order to speed up convergence, coefficients in the first guess state are estimated from ERA-
- 130 Interim analyses using the above equations. Surface spectral emissivity is represented in the state-
- 131 vector by a set of eigenvectors derived from the RTTOV emissivity atlas whose eigenvalues are co-
- 132 retrieved with other variables (Siddans et al., 2015).
- 133 For column average CO, agreement with CAMS re-analysis in multi-year time-series is generally
- 134 within ± ~10 ppbv (Figure S3). Vertical sensitivity of the CO retrieval is illustrated in Figure S4 which
- shows example averaging kernels as applied to the CAMS profiles for tropical land and mid-latitudesea.
- 137 In initial fits to IASI observations with the IMS extended scheme, systematic spectral residuals were
- 138 found (below 2000 cm⁻¹) which are significant compared to the instrument noise. These are
- accounted for in the retrieval by fitting two "spectral residual patterns", vectors b_0 and b_1 which
- 140 were derived by averaging the differences between observed and simulated spectra over sea in the
- 141 latitude range 60°S to 60°N (for 3 selected days in each season). These simulations adopted ECMWF
- analyses for temperature and water vapour and CAMS analyses for ozone and assumed no methanol
- 143 to be present. The difference spectra were analysed to obtain the mean residual spectrum (b_0) and
- 144 the spectrum of an additional component which varies linearly with off-nadir scan-angle (b_1). These
- 145 two fixed patterns were then added into the forward model for use in subsequent analyses:

146
$$F(\mathbf{x}) = R'(\mathbf{x}) - x_{b0}\mathbf{b_0} - x_{b1}\mathbf{b_1}$$

147

Equation 5

148 Where x_{b0} and x_{b1} are retrieved parameters (included in the state vector, with negligible prior 149 constraint). Vectors b_0 and b_1 are both fixed to zero in the CO fit window.

From **Equation 2**, it is straightforward to derive weighting function profiles, K_{gas} , for each minor gas (derivative of F(x) with respect to the number density at each level). Example weighting functions for the methanol spectral feature at 1034cm⁻¹ are shown in **Figure S5**.

153 It is important to note that infrared sensitivity to methanol varies greatly with height. Above the 154 surface, the weighting function is negative because methanol absorbs radiation emitted from the warmer surface. However, sensitivity is low near to the ground due to the very small difference 155 156 between the atmospheric temperature and that of the surface. If the surface temperature is lower 157 than the atmospheric layer above, the methanol weighting function in that layer will be positive. 158 Because the top-of-atmosphere spectral signature of methanol is strongly dependent on the 159 temperature profile and surface-air temperature contrast, the shape of the methanol reference 160 profile adopted in the fit is critical to the retrieved scale factor and hence column average mixing ratio. Adopting a constant mixing ratio with height as reference profile will result in a smaller column 161 162 average being retrieved than would be the case if the reference profile contained more methanol 163 near the surface. If methanol is assumed to be near the surface, where sensitivity is weak, then a 164 larger amount is needed to explain a given observed spectral signature than would be the case if the methanol is assumed to be at a higher, colder altitude, where the sensitivity is stronger. In order to 165 166 look at geographical and temporal variations consistently it is desirable to apply a retrieval scheme uniformly across the globe. Rather than tailor the shape of the reference profile according to 167 168 expectations from an emission inventory, the flat profile shape has therefore been adopted 169 everywhere. Over emission sources, however, methanol is usually located close to the surface, so it

170 is to be expected that this reference profile will lead to a lower column average being retrieved than 171 a realistic model would predict. This can be accounted for in model comparisons by applying

172 averaging kernels which characterise the sensitivity of the retrieved methanol column average to 173 perturbations in the true methanol profile:

174
$$A_{gas} = G_{x_{gas}} K_{gas}$$

175

176 Where the matrix K_{gas} contains the derivatives of the measurements with respect to methanol 177 profile perturbations at each of the vertical levels in the FM and $G_{x_{gas}}$ is the derivative of the retrieved methanol scale factor with respect to perturbations in the measurement vector. $G_{x_{aas}}$ is 178 179 one row of the retrieval gain matrix (containing the derivatives of each state vector element with 180 respect to perturbations in each measurement), given by the standard equation (Rodgers, 2000):

181
$$G = \langle K^t S_y^{-1} K + S_a^{-1} \rangle^{-1} K^t S_y^{-1}$$

Equation 7

Equation 6

182

198

199

Where **K** is the weighting function matrix giving the derivative of the forward model with respect to 183 184 all elements of the state vector (including the methanol scale factor). Figure S5 shows that because 185 $G_{x_{aas}}$ is a vector (same dimension as the measurement vector), the methanol averaging kernel A_{gas} 186 (dimension FM levels) has practically identical shape to the methanol weighting function, K_{gas} (though usually with reversed sign). Magnitudes of the elements of A_{gas} depend on the assumed 187 reference profile shape (because the elements of K corresponding to the methanol scale factor 188 189 depend on the profile shape).

190 A_{gas} can be used to estimate the column amount, $x_{iso:m}$, that the retrieval is expected to return given a model methanol concentration profile, n_m :¹ 191

$x_{meth:m} = A_{gas} n_m$

Equation 8

192 This accounts for the effects of varying vertical sensitivity and the profile shape assumed in the 193 retrieval. Because the reference profile shape is implicit to A_{gas} , changing that will change $x_{meth:m}$ 194 as well as the retrieved column average, but it will not change the relative agreement between the 195 two. (Changing the assumed profile shape simply scales both quantities.) 196

197 The solution error covariance matrix for an optimal estimation retrieval is given by:

$$S_x = \left(S_a^{-1} + K^T S_y^{-1} K\right)^{-1}$$

Equation 9

The estimated error on the retrieved methanol column average is given by the square-root of the 200 diagonal element of S_x which corresponds to x_{qas} . 201

The IMS extended scheme is applied to all scenes, irrespective of cloud, however the presence of 202 203 extensive, thick cloud limits retrieval quality and of course no information on minor gases such as CO or methanol is available below optically thick cloud. A simple test is used here: the difference in 204 brightness temperature between the IASI observed spectral radiance at 950 cm⁻¹ and that simulated 205 on the basis of temperature and humidity profiles and surface temperature interpolated from 206

¹ The prior constraint for the retrieved methanol scale factor is negligible so can be neglected in Equation 8.

ECMWF analyses is calculated. If this difference (observation – simulation) is outside the range of -5
 to 15 K, the scene is flagged as cloudy. These scenes are not used at all in the analysis reported here.

- 209 The scheme applied here therefore differs in a number of key respects from that applied to global
- 210 methanol retrieval from IASI reported by Razavi et al. (2011). Their scheme used brightness
- temperature differences between three channels near the methanol Q branch peak near 1034 cm⁻¹
- and six neighbouring channels where methanol absorption is low and conversions factors to
- 213 methanol column derived from optimal estimation retrievals using online line-by-line modelling.
- 214 Methanol is retrieved in four layers adopting a terrestrial and a marine profile as prior with
- variability from a chemical-transport model as covariance matrix diagonals and a long correlation
- 216 length for off-diagonals. It is also radically different from the neural net scheme employed by Franco
- 217 et al. (2018).

218 SM-3: Satellite Observed Methanol (CH₃OH)

219 Methanol (CH₃OH) infrared absorption features are much weaker than those of CO and background

- 220 levels of CH₃OH over ocean outside fire plumes are too low to be detectable in individual soundings
- above IASI's level of noise-equivalent spectral radiance (NESR), so retrieved values there are zero ±
- NESR. At locations of temperature inversion, where methanol spectral features appear in emission
- above a baseline of colder surface emission, retrieved scaling factors for the methanol reference
 profile are negative (see SM-1). Systematic errors, due for example to insufficiently accurate
- profile are negative (see SM-1). Systematic errors, due for example to insufficiently accurate
 handling of interference from neighbouring spectral lines, can also result in averaged CH₃OH being
- negative in these marine regions, though not significantly so in comparison to their estimated errors
- 227 (see SM-2, Figure S6). The white region in Figure S6 shows where we have filtered out retrievals
- with large errors (i.e. $>15.0\times10^{15}$ molecules/cm²). In the multi-month average (November-December
- 229 2019, January 2020) there still appears to be a negative offset in the IASI retrievals. For this work, we
- subtracted a negative background value of -3.68 ×10¹⁵ molecules cm⁻² from individual retrievals used
- in **Figure 4** and **Figure 5** of the main manuscript. This background value was based on data between
- the 1st and 17th January 2020 covering part of the North Pacific (135°E-115°W, 0-30°N).
- 233 Intercomparing the fire seasons (November-December-January, NDJ), IASI detects clear
- enhancements in TCCH₃OH during 2019/2020. Over Australia and South America (Figure S7a & c),
- TCCH₃OH ranges between 8.0-15.0 $\times 10^{15}$ molecules cm⁻² and 6.0-10/0 $\times 10^{15}$ molecules cm⁻², in both
- 236 NDJ 2018/2019 and 2019/2020. In the 2018/2019 fire season, background values (i.e. over the
- central South Pacific) between 0.0 and 3.0×10^{15} molecules cm⁻². The Hovmöller diagram (**Figure S7b**)
- shows peak TCCH₃OH between 8.0 and 12.0×10^{15} molecules cm⁻², which generally co-locate with
- total-column carbon monoxide (TCCO) (**Figure 2b** of the main manuscript) for the 2018/2019 fire
- season. However, in the 2019/2020 fire season, while continental values remain similar, mean outflow TCCH₃OH ranges between 3.0 and 8.0×10^{15} molecules cm⁻² (**Figure S7c**), while peaking
- outflow TCCH₃OH ranges between 3.0 and 8.0 $\times 10^{15}$ molecules cm⁻² (**Figure S7c**), while peaking above 15.0 $\times 10^{15}$ molecules cm⁻² in the Hovmöller diagram (**Figure S7d**), highlighting substantial
- variability. In both cases, the difference plots (**Figure S7e & f**) show large-scale enhancements in
- TCCH₃OH (1.5-5.0 ×10¹⁵ molecules/cm² and 5.0-10.0 ×10¹⁵ molecules/cm² in the seasonal and daily
- differences, respectively) over the South Pacific propagating as far as South America (differences
- 246 statistically significant at the 99% confidence level see **Figure S7e**).

247 SM-4: Satellite Observed Methane (CH₄)

- 248 **Figure S8** shows example daily IASI maps of column average CO and methane mixing ratios for 2nd
- and 10th January 2020. On both days, there are pronounced CO plumes substantially larger than the

- 250 background values. For CH₄ the spatial coverage is sparser due to the stringent cloud filtering and
- 251 other quality control needed for reliable retrieval of methane perturbations at the ~1% level.
- 252 Furthermore, CH₄ in airmasses arriving from tropical latitudes is elevated to levels comparable to
- 253 that in the fire plumes. These factors make it difficult to discriminate CH₄ enhancements due to the
- 254 Australian fires. Although certain CH₄ features are co-located with the main CO plumes, their spatial
- extent is restricted by the stringent cloud filtering, as evident in **Figure S8c & d** where the CO plume
- offshoot (150-180°E, 60-40°S) is not sampled in the case of CH_4 . In the main manuscript (i.e. **Figure**
- **4**) we have therefore limited attention to the daily time-series of a spatially averaged domain and
- the 2-week anomaly with reference to the deseasonalised, detrended decadal January mean.

259 SM-5: Enhancement Ratio Uncertainties

- 260 To test the robustness of the TCCH₃OH:TCCO enhancement ratios, we moderately perturbed some
- 261 of the subjective parameters used to derive these ratios. The key parameters were time length used
- to study the fire period, the in-plume threshold for TCCO and the in-plume threshold for TCCH₃OH.
- 263 The results are shown in **Table S1**, but overall we find that the derived enhancement ratios are
- 264 relatively insensitive to moderate perturbations to these parameters.

265 References

Alvarado, M. J., et al. (2010). Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B

and their impact on ozone: an integrated analysis of aircraft and satellite observations. *Atmos.*

- 268 *Chem. Phys.*, **10**, 9739-9760, doi:10.5194/acp-10-9739-2010.
- 269 Franco, B., et al. (2018). A General Framework for Global Retrievals of Trace Gases from IASI:
- 270 Application to Methanol, Formic Acid and PAN. J. Geophys. Res., **123**, 13963-13984,
- doi:10:1029/2018JD029633.
- Logan, J. A. (1983). Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, 88, 10785–10807, doi:<u>10.1029/JC088iC15p10785</u>.
- 274 Razavi, A., et al. (2011). Global distributions of methanol and formic acid retrieved for the first time
- from the IASI/MetOp thermal infrared sounder. *Atmos. Chem. Phys.*, **11**, 857-872, doi:10.5194/acp11-857-2011.
- Rodgers, C. D. (2000). Inverse Methods for Atmospheric Sounding: Theory and Practice, *World Sci.*,
 Hackensack, New Jersey, USA.
- Siddans, R., Gerber, D., Bell, B. (2015). Optimal Estimation Method retrievals with IASI, AMSU and
 MHS measurements. Final Report, EUM/CO/13/46000001252/THH.
- 281 Siddans, R., et al. (2018). RAL Infrared Microwave Sounder (IMS) temperature, water vapour, ozone
- and surface spectral emissivity. *Centre for Environmental Data Analysis*,
- 283 doi:10.5285/489e9b2a0abd43a491d5afdd0d97c1a4.
- Veefkind, J. P., et al. (2012). TROPOMI on the ESA Sentinel-5 Precursor: A GMES mission for global
- observations of the atmospheric composition for climate, air quality and ozone layer applications.
- 286 *Remote Sensing of Environment*, 120, 70-83. doi:10.1016/j.rse.2011.09.027.
- 287
- 288

289 Figures



290 291



lines represent the 3-month average. Panel e) represents regional 2018/2019 and 2019/2020 TCNO₂

weighted by 2019/2020 and 2018/2019 FRP, respectively.





299 Figure S2: Optical depth spectra in the intervals used by the IMS extended scheme to target a) CO

and b) CH_3OH . The black bars are IASI spectral channels used by the retrieval scheme.



Figure S3: Column average CO volume mixing ratio retrieved from MetOp-A by the extended IMS
 scheme in comparison with CAMS analyses. The plots show monthly mean values in 10° latitude bins
 from retrievals sampled 1 day in 10. The CAMS analyses have been sampled at locations of individual
 MetOp soundings. Panels a) represents the retrieval, b) is the CAMS with averaging kernel and *prior* term applied (CAMS x AK) and c) is the retrieval – CAMS x AK difference.











Figure S5: Vertical sensitivity of the CH₃OH retrieval: the figure shows temperature profiles for

tropical land and mid-latitude sea (left); CH₃OH weighting functions at 1034 cm-1 (centre) and
averaging kernels for the scale factor for the CH₃OH reference profile (constant 1 ppbv at all

altitudes). These are presented as the change in total column amount for a perturbation in layer

351 amount at each vertical level.

352

346



Figure S6: IASI TCCH₃OH errors (10^{15} molecules/cm²) for NDJ 2019/2020.



357

Figure S7: IASI NDJ total-column methanol (TCCH₃OH, 10¹⁵ molecules/cm²) for a) 2018/2019, c)
2019/2020 and e) difference 2019/2020-2018/2019. Green polygon-outlined regions in panel e)
represent statistically significant differences between the fire seasons at the 99% confidence level
(CL, based on the Student t-Test) and where absolute differences are greater than 1.0×10¹⁵
molecules/cm². Panels b), d) and e) represent Hovmöller diagrams of IASI TCCH₃OH from November
January at 155°E, between 70°S-0°S (black dashed line in panel a)), for 2018/2019, 2019/2020 and
the 2019/2020-2018/2019 difference, respectively. White (panels a-d) and grey (panels e & f) regions

represent missing data in the satellite record (i.e. average values with error terms > 15.0×10¹⁵
 molecules/cm²).



367
368
368
368
368
369
369
369
369
369
369
369
360
369
360
360
360
360
360
360
361
361
362
363
364
365
365
366
366
367
368
368
368
369
369
369
369
369
369
369
360
369
360
360
360
361
361
362
363
364
365
365
366
366
366
367
368
368
368
369
369
369
369
369
369
360
360
360
361
361
361
361
362
364
365
365
366
366
366
366
366
367
368
368
368
368
368
368
368
368
369
369
369
369
369
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360
360

Date	тссо	TCCH₃OH	Box 1	Box 2	Box 3	Box 4
	Threshold	Threshold				
	(molecules/cm ²)	(molecules/cm ²)				
1-17 Jan 2020	18 x10 ¹⁷	5 x10 ¹⁵	0.0036	0.0059	0.0091	0.0081
			±5.98%	±3.13%	±1.28%	±1.94%
25 Dec 2019-	18 x10 ¹⁷	5 x10 ¹⁵	0.0050	0.0053	0.0096	0.0083
20 Jan 2020			±4.41%	±3.55%	±1.29%	±2.11%
1-17 Jan 2020	16 x10 ¹⁷	5 x10 ¹⁵	0.0029	0.0051	0. 0096	0.0082
			±6.15%	±3.96%	±1.29%	±2.07%
1-17 Jan 2020	20 x10 ¹⁷	5 x10 ¹⁵	0.0029	0.0051	0.0096	0.0084
			±8.00%	±4.04%	±1.34%	±2.27%
1-17 Jan 2020	18 x10 ¹⁷	4x10 ¹⁵	0.0030	0.0052	0.0097	0.0085
			±7.11%	±3.61%	±1.23%	±1.94%
1-17 Jan 2020	18 x10 ¹⁷	6 x10 ¹⁵	0.0028	0.0049	0.0094	0.0081
			±7.10%	±4.41%	±1.39%	±2.32%

373

 73
 Table S1: IASI TCCH₃OH:TCCO enhancement ratios for the boxes in Figure 5a of main text with

374 perturbations to time period and TCCH₃OH:TCCO in-plume thresholds.