

Nitrous acid is a global driver of photochemistry in fresh wildfire plumes

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24 Nitrous acid (HONO) is an important precursor of the hydroxyl radical (OH), which controls the
25 degradation of pollutants, greenhouse gases, and contributes to photochemical smog. Due to
26 lack of wide scale measurements, pyrogenic HONO emissions are uncertain, and currently are
27 missing in most global models. Exploiting observations of the TROPOMI/Sentinel-5 Precursor
28 satellite sounder, we provide here the first global survey of atmospheric HONO that directly
29 addresses the need for wide scale measurements above and downwind of wildfires. Large,
30 unambiguous enhancements of HONO are consistently found in fresh wildfire plumes from
31 major ecosystems worldwide (savanna, grasslands, shrubland, tropical- and extratropical
32 forests). We derive averaged HONO/NO₂ enhancement ratios and show that these exhibit a
33 strong and systematic dependence on biome type. Supported by aircraft measurements, we
34 demonstrate that even the most recent assessments generally underestimate pyrogenic HONO
35 emissions by a factor of two to four across all ecosystem types. At the observed levels, HONO
36 photolysis accelerates oxidative plume chemistry that forms ozone and secondary organic
37 aerosol, and is responsible for two-thirds of OH production in fresh wildfire plumes worldwide.
38 Global model calculations indicate a potential substantial impact of pyrogenic HONO emissions
39 on atmospheric composition, enhancing ozone levels by up to 7ppbv regionally.

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41 As primary oxidant of the atmosphere, OH radicals control the degradation of pollutants and
42 greenhouse gases, and contribute to photochemical smog and ozone formation¹. HONO is a key
43 constituent of the tropospheric photochemistry, primarily as a source of OH. However, the HONO
44 budget remains poorly constrained², despite recent scientific progress³⁻⁷.

45 Biomass burning (BB) plays an important role in the global emission budget of reactive gases in
46 the atmosphere⁸. Fires can cause large perturbations to the chemistry and composition of the
47 atmosphere, affecting climate and leading to adverse effects on human health. Atmospheric
48 chemical transport models provide an ideal means of assessing these impacts, but require an
49 accurate representation of the chemistry in fire plumes as well as reliable ecosystem dependent
50 emission estimates that are usually based on fire activity data together with estimated emission
51 factors obtained from laboratory and in situ measurements^{9,10}.

52 Global models that assess the importance of HONO as OH precursor on the global scale¹¹ typically
53 neglect HONO from wildfires and thus provide lower limit estimates. Known formation
54 mechanisms of HONO in fire plumes include direct emissions¹², heterogeneous conversion of NO₂
55 on organic aerosols^{4,13} and on soot^{3,14}, photolysis of particulate nitrate¹⁵, hydrolysis of NO₂
56 dimers boosted in the presence of ammonia¹⁶. However, the relative importance of these
57 processes in fires and on the HONO to NO_x (NO+NO₂) emission factors have proven difficult to
58 quantify, especially on large scales, due to the lack of representativeness of measurements
59 performed in smoke chambers^{17,18} or collected in situ¹⁹⁻²⁴, and also because of the short
60 atmospheric lifetime of HONO. Global satellite sounders have revolutionized our knowledge on
61 the emission mechanisms and global distributions of many short-lived gaseous pollutants²⁵⁻²⁷.

62 HONO however, has hitherto been detected only once from space, namely in an exceptionally
63 large stratospheric smoke plume²⁸ using the Infrared Atmospheric Sounder Interferometer (IASI).
64 Here we show that the new satellite TROPospheric Monitoring Instrument (TROPOMI), launched
65 in 2017 onboard Sentinel-5 Precursor, is capable of observing HONO consistently in freshly
66 emitted wildfire plumes, providing information that is otherwise unavailable. To achieve this,
67 TROPOMI has two decisive advantages over its predecessors (such as the Ozone Monitoring
68 Instrument, OMI), namely a high spatial resolution (3.5x7 km²) and a higher signal-to-noise ratio.
69 Compared to infrared sounders, TROPOMI measures in the ultraviolet-visible domain and has a
70 much better sensitivity to HONO in the lowermost atmosphere.

71 **Global pyrogenic HONO probed from space**

72 Daily global HONO slant column densities (SCD, or the integrated concentration along the light
73 path) were retrieved from TROPOMI radiance spectra (Methods) using Differential Optical
74 Absorption Spectroscopy^{29,30} (DOAS). A typical example is shown in Fig. 1a for wildfires in British
75 Columbia (Canada), along with unambiguous spectroscopic evidence for the presence of HONO
76 in the selected TROPOMI observation (inset in Fig. 1a). Inspection of the daily HONO maps reveals
77 consistent large local enhancements near the fire sources similar to enhancements of nitrogen
78 dioxide (NO₂) SCD that are co-retrieved in the same wavelength range (Supplementary Fig. S1a).
79 This suggests that HONO is either directly emitted from fires or very rapidly formed by pyrogenic
80 precursors. The geographical extent of the observed HONO plumes is generally limited to a few
81 tens of kilometers downwind of the fires, reflecting the short atmospheric lifetime of HONO
82 (order of 15 minutes in clear air³¹, longer in smoke plumes) and the rapidly changing conditions
83 as the plumes age and dilute. We have analyzed one full year of global measurements between
84 May 2018 and April 2019. Based on conservative selection criteria (Methods), we isolated a total
85 of 5093 TROPOMI pixels with unambiguous HONO detection, all coinciding with wildfire plumes,
86 as readily confirmed by TROPOMI-retrieved distribution of other pyrogenic compounds including
87 carbon monoxide (CO), NO₂, formaldehyde (HCHO), glyoxal (CHOCHO), and aerosols (see
88 examples in Supplementary Fig. S1). These HONO observations (Fig. 1b) are located over
89 dominant BB regions, as evidenced from the data of GFED (Global Fire Emissions Database³²;
90 Supplementary Fig. S2a), allowing the first meaningful assessment of HONO emissions from fires
91 in a global context.

92 **Comparison with aircraft observations**

93 The TROPOMI HONO measurements are corroborated by comparisons with aircraft HONO
94 column observations acquired during the Biomass Burning Fluxes of Trace Gases and Aerosols
95 (BB-FLUX) field study conducted in the US Pacific Northwest during the summer of 2018 wildfire
96 season (Methods). Here we use measurements of the wildfire plume from the Rabbit Foot Fire,
97 Idaho, on August 12, 2018. The aircraft, equipped with a zenith-sky DOAS instrument, flew under

98 the smoke layer and performed two traverses of the plume, nearly synchronized with TROPOMI.
99 HONO and NO₂ are retrieved using identical fit settings as used by the satellite. The HONO SCDs
100 derived from the aircraft measurements provide independent corroborating evidence for the
101 presence of HONO in large amounts at the same location as the satellite observations (Fig. 2a).
102 Notably, the aircraft measurement integrates HONO and NO₂ over the entire wildfire plume,
103 while the satellite measurement primarily samples the top layer of the plume (Supplementary
104 Fig. S3). The higher HONO SCD measured from the aircraft reflects the fact that all photons that
105 reach the plane have traversed the entire plume. For comparison with the satellite, we compare
106 the enhancement ratios of the measured HONO SCD to the NO₂ SCD (RHN) to cancel differences
107 in Air Mass Factors (AMFs) that arise from the different sampling geometries. The RHN
108 cancellation of AMFs is justified because both gases are retrieved in the same wavelength range
109 (Methods), as long as the HONO and NO₂ profile shapes in the plume are similar (see
110 Supplement). Similar profile shapes are expected since both are photolabile species.
111 Furthermore, the RHN is independent of the trace gas dilution during transport, and a useful
112 metric^{33,18} of the photochemical production rate of HONO.

113 Comparisons of TROPOMI and aircraft RHNs are presented in Figs. 2b and 2c. The satellite RHNs
114 (0.33-0.54) agree very well with the aircraft values (0.29-0.54) after the data are aligned along a
115 common plume age axis (Methods). There is no satellite bias discernible within the low (<10%)
116 measurement error of the aircraft data. Two additional BB-FLUX research flights (Supplementary
117 Fig. S4) show similarly good agreement over a wider range of RHN values, further supporting the
118 assumption of similar HONO and NO₂ profile shapes inside the plume. The aircraft data reveals
119 variability in RHN on fine spatial (few 100m) and temporal scales (seconds to minutes) that
120 cannot be resolved from space. Notably, comparing aircraft column observations with columns
121 from space actively bridges the different spatial scales to the best degree possible, though
122 atmospheric variability remains a limiting factor. Overall, Fig. 2c and Supplementary Fig. S4
123 illustrates that the aircraft data approximate the satellite measured RHN best when near
124 synchronous observations of similar plume ages are compared.

125 **Uncertainties in HONO and NO₂ SCDs and RHN**

126 No statistically significant bias in the satellite RHN is observed (6±8 %, Supplementary Table S1),
127 reflecting identical HONO and NO₂ retrieval settings and cross-section spectra used for both
128 aircraft and satellite (known to better 6% and 5%, Supplementary Table S1). However, a common
129 systematic error cannot be fully excluded either. For TROPOMI global observations, the RHN
130 systematic uncertainty is of ±25%. Contribution of SCDs random errors to biome averaged RHN
131 values (as in Table 1 below) is negligible due to the large number of HONO detections.
132 Furthermore, the RHN variability within a satellite ground pixel is found to be highly significant
133 in the aircraft data, and similar to the variability between nearby satellite detections (Fig. 2c, and
134 Supplementary Fig. S4). Interestingly, the satellite bias is insignificant also within the ±6.9%

135 uncertainty of the aircraft data (accuracy in RHN, excluding cross-sections errors). This suggests
136 that plume heterogeneity is not limiting the comparison between both remote sensing platforms,
137 and reflects the benefits of more direct comparison by sampling over extended spatial scales.

138 **Enhanced HONO relative to NO₂ surveyed worldwide**

139 In Figs. 2b and 2c, it is noteworthy that TROPOMI RHN significantly increases (to values as high
140 as 1.2) for pixels near the fire sources. This feature is commonly observed for the fires globally,
141 and is directly the result of elevated HONO SCDs (rather than low NO₂ SCDs) near the fires
142 (Supplementary Fig. S5). This suggests that HONO primary emissions either dominate over
143 secondary sources, or cannot easily be separated from fast secondary formation close to the
144 fires. From the global detections, distinct spatial patterns of RHN clearly emerge (Fig. 3a) that are
145 attributable to the distribution of ecosystems. Observed RHNs (10th-90th percentile) tend to be
146 lower (0.14-0.61) over regions dominated by fires from grassland, savannas and open shrubland
147 (Kazakhstan, most of Africa and Australia), intermediate values (0.23-0.62) are found over
148 tropical deciduous forest fires (Central and South America, mainland Southeast Asia, the eastern
149 coast of Australia, and east of Madagascar), and the highest values (0.32-0.78) correspond to
150 extra-tropical evergreen forest burns (USA, Canada and far Eastern Russia). This dependence of
151 RHN on vegetation type matches findings of earlier studies (Table 1). However, the TROPOMI
152 RHN is a factor of 2-4 higher compared to most values found in the current literature¹⁰, regardless
153 of the vegetation type. This is highly significant, and well outside the measurement uncertainty.
154 Because of its detection limit, satellite data is more representative of large wildfires
155 (Supplementary Fig. S2b) but the finding of high RHNs is robust over the complete range of fire
156 emissions covered by TROPOMI HONO measurements (Supplementary Fig. S2c). For savanna
157 fires, a statistically significant anti-correlation between the fire strength and RHN is observed,
158 consistent with strong savanna fires emitting larger amounts of NO_x. Our results suggest that
159 global HONO production from fires has been significantly underestimated, and we present
160 several reasons for this. First, the published RHN estimates from field studies (see Supplementary
161 Table S2) are based on in situ measurements most often for modest burns, optically thin BB
162 plumes (thus very different than the fire emissions sampled by TROPOMI and BB-FLUX), and
163 sampled away from the core of fire plumes. This is supported by recent in situ observations of
164 high RHN in fresh plumes from large fires³⁵. Second, the highly polluted conditions in sizeable fire
165 plumes likely favor the conversion of NO₂ to HONO through heterogeneous processes^{3,13,16} as
166 well as NO₂ loss, for instance from peroxyacetyl nitrates (PANs) formation. These effects would
167 be seen more in the distal rather than the proximal part of the plume, so that such a potential
168 bias can only explain part of the observed discrepancy. Third, the higher RHNs derived from
169 TROPOMI observations likely reflect the ability to sample freshly emitted, almost undiluted
170 plumes inside the zone surrounding fires that is hardly accessible to research flights, because of
171 fire-induced atmospheric turbulence, and/or due to temporary flight restriction (TFR) zones. A

172 clear decrease is observed for RHN, HONO and NO₂ with increasing distance from the fires
173 (Supplementary Fig. S5). This presents direct evidence for the difficulty of establishing emission
174 factors for highly reactive species from field measurements downwind of fires in rapidly evolving
175 plumes, whose composition changes on short temporal and spatial scales. Fourth, emission
176 factors determined from smoke chamber experiments (Table 1) are obtained under specific
177 atmospheric mixing and photochemical conditions that prevail in the laboratory settings, and
178 that are likely different from the conditions found in actual wildfires (in terms of fuel
179 heterogeneity, wind fields, humidity gradients, fire strength, fuel consumption rates, pyrolysis
180 contributions, etc.). Consistent with this hypothesis, our evidence that RHN depends on fire
181 strength of savanna fires (Supplementary Fig. S2c) corroborates previous findings³⁶ that burn
182 conditions modify fire emissions.

183 **HONO as the main source of OH in fresh smoke plumes**

184 The importance of HONO for atmospheric chemistry in fire plumes is further demonstrated by
185 contrasting the calculated production rates of OH due to HONO photolysis with the
186 corresponding estimated production rates due to other known pyrogenic sources of OH,
187 including the photolysis of ozone in presence of H₂O, the photolysis of 16 oxygenated volatile
188 organic compounds (OVOCs), and the ozonolysis of 12 alkenes (Methods). Constrained by
189 TROPOMI measurements, we estimate the relative contributions of the most important
190 precursory compounds to the total OH production in fresh wildfire plumes worldwide, leveraging
191 the fact that relative contributions are independent of assumptions about aerosol optical
192 properties and plume optical thickness to first order (Methods). On average for all wildfire
193 plumes detected by TROPOMI, the photolysis of HONO accounts for 63±16% of the total OH
194 production, and more than 80% locally (Fig. 3b); the error bar accounts for uncertainties in the
195 abundances of the contributing compounds and in their rates and OH yields. The photolysis
196 of all OVOCs accounts collectively for 35% (HCHO: 18%, CHOCHO: 4%, other OVOCs: 13%), and
197 other sources for 3% (ozone photolysis: 1%, alkenes ozonolysis: 2%) of the total OH production
198 from fires. The daytime contribution of HONO obtained here is much higher than previously
199 reported (12-34%), for urban conditions^{37, 38} and forest canopy³⁹. This makes HONO the main
200 precursor of OH in fresh fire plumes; this finding is supported on a local scale, by reported large
201 OH production due to HONO from western US wildfires³⁵. Under the simplifying assumption that
202 pyrogenic HONO is directly emitted, its impact on other atmospheric compounds is also
203 substantial. We estimate concentration enhancements of up to 30% for OH and 10% for O₃ with
204 global model simulations (Supplementary Fig. S6). Pyrogenic HONO emissions also represent a
205 significant input to the global NO_x budget, estimated at ca. 1 TgN yr⁻¹.

206 We have demonstrated the first global HONO observations from space. The detailed study of
207 further HONO observations – including from geostationary platforms – in connection with
208 models and additional atmospheric and fire activity data, holds largely unexplored potential to

209 provide valuable insights into the still poorly understood formation mechanisms of HONO, and
210 its importance for atmospheric chemistry and climate in the global context of wildfires and
211 possibly also urban air.

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323 METHODS

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325 TROPOMI retrieval of HONO and NO₂

326 TROPOMI⁴⁰ is the single-payload of the Sentinel-5 Precursor platform launched in October 2017.
327 It is a nadir-viewing remote sensing instrument measuring the solar radiation reflected by the
328 Earth and backscattered by its atmosphere. TROPOMI has heritage from OMI⁴¹ and the SCanning
329 Imaging Absorption spectroMeter for Atmospheric Cartography⁴² (SCIAMACHY). The instrument
330 is a push-broom imaging spectrometer with eight spectral bands covering ultraviolet to
331 shortwave infrared wavelengths with a spectral resolution of 0.25–1 nm and a spectral sampling
332 ratio of 2.5–6.7. Flying in a low-Earth early afternoon polar orbit with a wide swath of 2600 km
333 resulting in daily global coverage, it delivers vertically integrated abundances of key atmospheric
334 constituents (O₃, NO₂, SO₂, HCHO, CHOCHO, CO, CH₄) complemented by cloud and aerosol
335 information, at the resolution of 3.5x5.5 km² (from 6 August 2019) or 3.5x7 km² (this study,
336 compared to 13x24 km² and 30x60 km², for OMI and SCIAMACHY, respectively).

337 For this work, we analyze ultraviolet-visible spectral data measured between 1 May 2018 and 30
338 April 2019, and solar zenith angles lower than 65°. The HONO slant column density (SCD, in
339 molecules cm⁻²) is retrieved from each recorded radiance spectrum using the established
340 technique of Differential Optical Absorption Spectroscopy³⁰ (DOAS). In brief, the measured
341 spectrum is modeled using a reference spectrum, absorption cross-sections of relevant trace
342 gases, and radiance closure terms. The fitted parameters for the trace gases are the SCDs and
343 represent the corresponding concentrations integrated along the mean optical light path in the
344 atmosphere. Here the retrieval scheme is an adapted version of the TROPOMI HCHO algorithm⁴³.
345 We have followed recommended settings⁴⁴ and used a wavelength interval of 337–375 nm
346 optimized for HONO (see details in Supplementary Table S3). In the same spectral fitting step,
347 the slant column of NO₂ is retrieved. Given the relatively low peak-to-peak absorption of NO₂ in
348 the ultraviolet, the noise on retrieved NO₂ SCDs is larger than in the visible range⁴⁵. However, the
349 signal is such that there is no difficulty to detect NO₂ in wildfire plumes. To determine enhanced
350 NO₂ SCD for the fire plumes, a stratospheric NO₂ correction is applied, and is estimated using
351 measurements at the same latitude from over a sector (see Supplementary Table S3) with
352 negligible tropospheric NO₂ contribution⁴⁶.

353 Determination of the vertical column density (VCD, vertically integrated concentration) from the
354 measured SCD requires radiative transfer simulations to derive air mass factors (AMF, where
355 AMF=SCD/VCD). The AMF simulates the trace gas concentration integrated along the complex
356 photon path in the plume, relative to the vertical path. Here, the AMF can be formulated⁴⁷ by:

$$357 \quad AMF = \int b_{AMF}(z) \cdot N(z) \cdot dz \quad (1)$$

358 where $N(z)$ is the normalized concentration profile of the trace gas of interest and bAMF is the
359 height-resolved AMF (referred as box-AMF) that contains all dependences to parameters
360 (wavelength, geometry, surface reflectance, clouds, aerosols, etc.) influencing the vertical
361 sensitivity of the measurement, except $N(z)$. In case of HONO and NO_2 from fires, a general AMF
362 computation applicable globally is difficult because crucial input parameters are poorly known,
363 notably the trace gases vertical distribution and the aerosol optical properties and extinction
364 vertical profile (impacting bAMF).

365 We have calculated the ratio of HONO to NO_2 , a proxy for HONO production, independent of the
366 dilution of the trace gases during transport. Since NO_2 and HONO are jointly retrieved in the same
367 spectral region, the box-AMFs can be considered identical for both species. Under the
368 assumption that HONO and NO_2 have the same profile shapes (which is supported by our
369 validation results, Fig. 2c), in first approximation, the AMFs of HONO and NO_2 are the same (Eq.
370 1). We can therefore formulate RHN independently of the error-prone AMFs:

$$371 \quad \text{RHN} = \text{VCD}_{\text{HONO}}/\text{VCD}_{\text{NO}_2,\text{corr}} \approx \text{SCD}_{\text{HONO}}/\text{SCD}_{\text{NO}_2,\text{corr}} \quad (2)$$

372 where SCD_{HONO} is the HONO SCD, $\text{SCD}_{\text{NO}_2,\text{corr}} = \text{SCD}_{\text{NO}_2} - \text{SCD}_{\text{NO}_2,\text{strato}}$ is the retrieved NO_2 SCD
373 (SCD_{NO_2}) corrected for its stratospheric contribution ($\text{SCD}_{\text{NO}_2,\text{strato}}$). An error budget on SCDs and
374 RHN is given in Supplementary Table S1. In particular, the estimated RHN error from imperfect
375 cancellation of AMFs (due to wavelength dependence) is less than $\sim 1\%$.

376 For a quantitative comparison of the TROPOMI RHN, nearly synchronized aircraft remote-sensing
377 observations of HONO and NO_2 SCDs were used (see below). Conversely, the comparison of
378 TROPOMI column-based RHN with aircraft in situ concentration RHN measurements is not
379 considered here, as it is unlikely to carry much meaning, given the inhomogeneity of HONO and
380 the fundamental difference in air mass sampling of the two techniques.

381 To identify global HONO plumes and study source regions in a systematic and consistent way, a
382 set of criteria was formulated that can be satisfactorily applied globally without the need for
383 external fire data sources. Cloud information is not used either as it could lead to statistical bias,
384 for example by filtering pyrocumulus clouds. After removing obvious outliers (based on fitting
385 residuals), a detection test is applied: first, only satellite data over land are considered. Secondly,
386 satellite data are kept when $\text{SCD}_{\text{HONO}} > 3 \times \text{SCDE}_{\text{HONO}}$ (where $\text{SCDE}_{\text{HONO}}$ is the HONO SCD uncertainty
387 from the fit) and if at least one neighboring pixel satisfies the same criterion. An additional
388 selection of the pixels with $\text{SCD}_{\text{NO}_2,\text{corr}} > 3 \times \text{SCDE}_{\text{NO}_2}$ (where $\text{SCDE}_{\text{NO}_2}$ is the NO_2 SCD uncertainty
389 from the fit) is also applied, to improve the selectivity of wildfire plumes and to stabilize RHN.
390 However, the resulting pixels selection leads to elevated false HONO detections over regions with
391 large anthropogenic NO_2 signal. Therefore, a final and conservative selection criterion on
392 $\text{SCD}_{\text{HONO}} > 4 \times 10^{15}$ molecules. cm^{-2} is used to retain only the unambiguous pyrogenic HONO
393 detections. Applying these rather strict criteria to one year of TROPOMI data yields a set of 5093

394 usable HONO ground pixel detections, all located over biomass burning areas, giving additional
395 confidence in the selection approach.

396 **Aircraft measurements**

397 The Biomass Burning Fluxes of Trace Gases and Aerosol (BB-FLUX) field campaign took place
398 during the summer of 2018 wildfire season in the Pacific Northwest around Boise, ID, USA. The
399 University of Wyoming King Air research aircraft was equipped with remote sensing and in situ
400 instruments, including the University of Colorado Zenith Sky DOAS (CU ZS-DOAS) instrument,
401 which performed measurements of NO₂, HONO, HCHO and CHOCHO using scattered solar
402 photons in the zenith geometry. The aircraft was deployed underneath, inside and above the
403 wildfire plumes to measure column enhancements, wind speed, and plume vertical structure.
404 HONO and NO₂ differential SCDs were retrieved using the same fit settings as TROPOMI
405 (Supplementary Table S3). The background on either side of the plume was linearly interpolated,
406 and subtracted to derive trace gas SCD enhancements inside the plume. A total of 37 research
407 flights (RFs) were conducted, studying wildfires in Idaho, California, Oregon, Nevada, Utah and
408 Washington. A small subset of the BB-FLUX flights actively coordinated locating the plane
409 below/near wildfire plumes at the TROPOMI overpass times. In particular, BB-FLUX RF11 on 12
410 August 2018 targeted the Rabbit Foot Fire in central Idaho close in time to the S5P overpass
411 (~20:45 UTC). The aircraft conducted two plume underpasses between 20:00 and 20:15 UTC 50
412 km downwind of the fire. Two additional flights were used for comparison with TROPOMI, BB-
413 FLUX RF13 on 15 August 2018 for the same Rabbit Foot Fire, and BB-FLUX RF15 on 19 August
414 2019 over the Watson Creek Fire (Oregon). For the two flights, the aircraft traverses sampled the
415 wildfire plume at the S5P overpass time ±15 minutes.

416 Although the satellite and aircraft HONO SCDs presented in this study agree well qualitatively, a
417 thorough comparison is not straightforward because of differences in spatial-temporal sampling
418 of the air masses sounded by the two instruments, which have very different fields of view.
419 Furthermore, because of different observation geometries, the retrievals have different
420 sensitivity (light penetration) in the respective atmospheric vertical layers, in particular for large
421 aerosol optical depths. We have estimated this effect using the radiative transfer model LIDORT⁴⁸
422 version 2.7. A set of AMFs were calculated at a wavelength of 355 nm for typical BB plumes.
423 Because HONO (or NO₂) and aerosols are co-emitted, their vertical profiles were assumed to have
424 the same shape modelled by a Gaussian peaking at 2km above the surface, with full width at half
425 maximum of 0.5km. Biomass burning aerosols were represented by a bi-modal log-normal
426 particles size distribution⁴⁹, with a single scattering albedo between 0.8 and 0.9, indicative of
427 fresh to aged BB aerosols. Supplementary Fig. S3 shows an example of the dependence of the
428 AMFs with aerosol optical depths (AOD). It illustrates the expected change in measurement
429 sensitivity due to aerosols⁵⁰ and the inherent differences of AMF between aircraft and satellite
430 measurements.

431 To evaluate the TROPOMI RHN estimates, we have calculated RHN from the aircraft HONO and
432 NO₂ SCDs data, for NO₂ background corrected SCDs larger than 5×10^{15} molecules.cm⁻². An error
433 analysis of SCDs and RHN is given in Supplementary Table S1. The advantages of comparing RHNs
434 are that they do not vary with the AMFs, and that RHN is independent of the horizontal
435 resolution. However, a time difference exists between aircraft and TROPOMI measurements (30-
436 45 minutes in case of RF11, less than 15 minutes for RF13 and RF15), and a time adjustment is
437 needed when comparing the aircraft and satellite RHNs. For this, we have estimated the age of
438 the plume separately for the aircraft and TROPOMI measurements, using trajectory calculations
439 made with the FLEXPART-WRF⁵¹ model. The Global Fire Assimilation System of the Copernicus
440 Atmosphere Monitoring Service⁵² (CAMS GFAS) was used for fire locations, plume injection
441 heights and emitted amounts. We released around 1×10^5 'particles' from each fire location and
442 followed each particle on its path through the atmosphere, tracking the time since its release.
443 Processes like turbulence were allowed to act stochastically on each particle to modify its
444 trajectory. Our dispersion calculations result in plume age spectra for each model grid box, which
445 we then sampled along the flight path of the aircraft and the locations of the TROPOMI
446 measurements. The mass-weighted mean of the age spectrum is used as best-guess for plume
447 age; its standard deviation allows to identify contamination by the Goldstone fire downwind (Fig.
448 2), and the corresponding data were removed from the analysis. At the edges of the plume, the
449 estimated plume age was sometimes found unrealistic due to very low particles concentrations,
450 and the respective data were not considered in the comparison. In total, seven TROPOMI pixels
451 (out of 40) were filtered out in Fig. 2c.

452 Calculation of OH production rates

453 The OH production rates were calculated for every TROPOMI pixel where HONO was detected,
454 using model-estimated photolysis rates. The sources of OH considered include photolysis of
455 HONO, O₃ and oxygenated VOCs, and ozonolysis of alkenes. HONO, HCHO and CHOCHO mixing
456 ratios were based on TROPOMI retrievals while concentrations of other VOCs were estimated
457 from TROPOMI-derived HCHO and enhancement ratios ($\Delta(\text{VOC})/\Delta(\text{HCHO})$) based on field data.
458 The calculation of concentrations requires assumptions on vertical profiles of the constituents
459 and AMFs (see below). Since these parameters are very uncertain (Supplementary Fig. S3), large
460 uncertainties in OH production rates are expected; however, these assumptions have little
461 impact on the relative contribution of HONO to the total OH production rate presented here, as
462 the vertical profiles of HONO and pyrogenic VOCs are expected to be very similar in the BB
463 plumes.

464 The concentrations of HONO, HCHO and CHOCHO at the assumed plume peak altitude of 2km
465 were estimated from TROPOMI measurements of these compounds, using the fixed vertical
466 profile described above. The corresponding HCHO and CHOCHO SCDs (see example maps in
467 Supplementary Fig. S1) are extracted from the TROPOMI HCHO offline product⁴³ and the

468 scientific TROPOMI CHOCHO product (adapted from GOME-2 CHOCHO retrievals⁵³). Details on
469 the DOAS settings are provided in Supplementary Table S3. The calculations were performed for
470 an assumed AMF of 0.5 for HONO and HCHO. An AMF of 1 is used for CHOCHO as radiative
471 transfer test simulations (described above) demonstrated twice the measurement sensitivity in
472 the visible part of the spectrum (where glyoxal is retrieved) than in the ultraviolet. The estimated
473 uncertainty on HCHO concentrations (relative to those of HONO) is ca. 27%, resulting from an
474 SCD uncertainty⁴³ of 10% and AMF errors related to differences in vertical profiles (20%) and in
475 the wavelength ranges of the retrievals (15%), based on radiative transfer model sensitivity
476 calculations. The CHOCHO concentration uncertainty (30%) is assumed to be similar to that of
477 HCHO.

478 The photolysis rates were obtained from the MAGRITTE chemistry-transport model^{54,55}, which
479 relies on the TUV photorate calculation package⁵⁶ with meteorological and other fields (pressure,
480 temperature, surface downward solar radiation, total ozone columns) derived from ECMWF ERA-
481 Interim reanalyses⁵⁷. Potential misrepresentation of the effects of clouds and aerosols might lead
482 to significant uncertainties in the photorates, but with little influence on their relative
483 magnitudes and therefore on the relative contributions of the different photolytic processes. The
484 uncertainty of the relative contribution of non-photolytic processes (alkene ozonolysis) is
485 increased due to these effects, by an assumed factor of 2, with very little impact on the overall
486 uncertainty of HONO contribution.

487 A constant ozone mixing ratio of 50 ppbv was assumed, whereas H₂O and temperature were
488 obtained from ECMWF. Uncertainties in O₃ and H₂O are significant but have little bearing on the
489 conclusions, as O₃ photolysis and alkene ozonolysis contribute for only a few percent of the total
490 OH source.

491 Besides OH formation due to HONO and O₃ photolysis, the photolysis of organic compounds
492 (primarily carbonyls) and the ozonolysis of alkenes generate OH radicals as well as HO₂ and RO₂
493 radicals which are partially converted to OH, depending on photochemical conditions³⁸. Biomass
494 burning plumes are usually characterized by high NO_x levels, typically in the ppbv range⁵⁸. In the
495 TROPOMI pixels where HONO has been detected and quantified, the estimated median NO₂
496 volume mixing ratio is ~25 ppbv at the peak of the plume, when assuming an AMF of 0.5.
497 Adopting an NO/NO₂ ratio of 0.2, based on airborne measurements in BB plumes during the
498 ARCTAS campaign over boreal forests^{59,60}, the resulting NO concentrations (~5 ppbv) are such
499 that HO₂ radicals produced in the plume are almost completely (>99%) converted to OH. The
500 same applies to non-acyl RO₂ radicals, converted to HO₂ and then OH. For acylperoxy radicals
501 (ACO₃), however, formation of PAN-like compounds through ACO₃+NO₂ is dominant, and only
502 ~30% of these radicals are converted to OH, based on reported rates⁶¹ for ACO₃+NO and
503 ACO₃+NO₂ (for lower tropospheric conditions and NO/NO₂=0.2).

504 The VOC photolysis processes considered here are listed in Supplementary Table S4 along with
505 their corresponding OH yield, assuming conversion efficiencies of 100% for HO₂ and for non-acyl
506 peroxy radicals, and 30% for acylperoxy radicals. These yields are based on the Master Chemical
507 Mechanism^{62,63} (MCM) v3.3.1 (<http://mcm.leeds.ac.uk/MCM>). The photorates (relative from that
508 of HCHO) were estimated using TUV, with photolysis parameters from MCM. For furfural, the OH
509 yield is assumed, and the photorate was calculated using published absorption cross sections⁶⁴
510 and a quantum yield⁶⁵ of 0.01, of the same order as for methacrolein and methylvinylketone⁶⁶.

511 The alkene ozonolysis processes considered here are listed in Supplementary Table S5 along with
512 their reaction rate and estimated OH yield, under the same assumptions as above. The reaction
513 rates and products are obtained from MCM v3.3.1. Monoterpenes are speciated as 25% α -pinene
514 and 75% β -pinene based on measurements in BB plumes during ARCTAS⁵⁹. The Supplementary
515 Table S5 also provides the estimated OH production due to the reaction ($P_{OH}(VOC+O_3)$) for a given
516 amount of the VOC (1 ppbv) and 50 ppbv O₃.

517 As noted above, the HCHO and CHOCHO concentrations were constrained by TROPOMI
518 observations. The concentrations of the other pyrogenic VOCs were estimated using VOC/HCHO
519 enhancement ratios (Supplementary Table S6) obtained from the review of emission factors¹⁰.
520 The enhancement ratio of two compounds is defined as the ratio of the excess concentrations of
521 the two compounds in the fire plume, relative to their ambient background concentrations.
522 Enhancement ratios relative to CO or CO₂ are routinely used to estimate biomass burning
523 emission factors⁸ (in g per kg dry matter). Here the molar enhancement ratios relative to HCHO
524 are calculated as $ER(VOC) = (EF(VOC)/MW_{VOC}) / (EF(HCHO)/MW_{HCHO})$, where EF denotes the
525 emission factor (g.kg⁻¹) and MW denotes molecular weight (g.mole⁻¹). Note that the natural
526 variability of emission rates and the role of secondary chemistry (chemical production and losses
527 within the plume) imply a large variability of enhancement ratios; in particular, the ratios depend
528 on plume age and photochemical conditions. Furthermore, many minor oxygenated VOCs are
529 either not measured or have so far unknown impacts due to lack of mechanistic information (e.g.
530 furfurals).

531 Supplementary Table S7 gives the estimated contributions of VOC photolysis reactions to the
532 production of OH, relative to the contribution of HCHO, as well as their estimated uncertainties.
533 Those relative contributions are calculated as:

$$534 P_{OH}(VOC)/P_{OH}(HCHO) = (\Delta VOC/\Delta HCHO) \times J_{VOC}/J_{HCHO} \times Y_{OH}(VOC)/Y_{OH}(HCHO) \quad (3)$$

535 where the enhancement ratios ($\Delta VOC/\Delta HCHO$) are given in Supplementary Table S6, and the
536 photolysis rates and OH yields are given in Supplementary Table S5. Although there is some
537 variation between VOC enhancement ratios according to fire type (extratropical forest,
538 temperate forest, tropical forest, savanna), the combined contribution of all VOC+hv reactions
539 (besides HCHO+hv) is relatively uniform across fire types, and is of the same order as that of

540 HCHO. When excluding the contribution of HCHO and CHOCHO (for which TROPOMI retrievals
541 are available), the contribution of VOC+hv can be approximated as 75±66% of the HCHO+hv
542 contribution. The main contributing species are, besides HCHO and CHOCHO, methylglyoxal and
543 biacetyl. Each of those two compounds contributes ~15-40% relative to formaldehyde.

544 Supplementary Table S8 provides the contribution of alkene ozonolysis to OH production, for
545 given levels of O₃ and HCHO in the plume, calculated as the product of the enhancement ratio
546 (Supplementary Table S6) by P_{OH} (Supplementary Table S5). The total production of OH due to
547 alkene ozonolysis is highest for temperate and boreal forest fires, due to their high emissions of
548 monoterpenes. Based on these results, the OH production rate per ppbv of HCHO is taken equal
549 to 23±17 pptv.h⁻¹ in Tropical regions, and 42±62 pptv.h⁻¹ elsewhere, in the calculation of the
550 overall OH production rate in TROPOMI pixels.

551 **Modelled global impact of pyrogenic HONO**

552
553 MAGRITTE v1.1⁵⁵ was run at 1°×1° resolution to estimate the impact of pyrogenic HONO on global
554 composition during summer 2018. Meteorology is obtained from ECMWF ERA-Interim. The
555 model includes a detailed representation of biogenic and pyrogenic VOC oxidation^{67,55}. The
556 photolysis rate calculation relies on TUV, with daily aerosol optical depth distributions from CAMS
557 (<https://ads.atmosphere.copernicus.eu>). Biomass burning emissions are calculated based on
558 GFED4³² (van der Werf, 2017) with emission factors from recent assessment¹⁰.

559 Two 6-month runs (March-August) were conducted, with and without pyrogenic HONO. Gas-
560 phase HONO formation and loss are included in both simulations. The pyrogenic HONO emission
561 factors are 1.10, 1.36, 2.29 g per kg of dry matter for savanna, tropical forest and extra-tropical
562 forest fires, respectively, based on the RHN from Table 1 and NO_x emission factors¹⁰, the NO/NO₂
563 ratio being taken equal to 0.2 (see above).

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652

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665 information it contains.

666

667 **Author contributions**

668 N.T., R.V., J.-F. M. designed research, M.V. supervised the work. N.T, I.D., C.L., H.Y., M.V.
669 developed the satellite algorithms and processed the data. K.J.Z., N.K., H.F., T.K.K., C.F.L., R.V
670 performed aircraft measurements and data analysis. J.-F. M., C.K. performed model calculations.
671 All authors contributed to the text and interpretation of the results. N.T. analyzed and
672 interpreted the TROPOMI HONO data, with the help of R.V. and K.J.Z. N.T. prepared all figures
673 and wrote the manuscript, with input from all coauthors.

674 **Competing interests**

675 The authors declare no competing interests.

676 **Additional information**

677 **Supplementary information** accompanies this paper.

678 **Data availability**

679 The global data and validation data that support the findings of this study are available in the
680 BIRA-IASB Data Repository (<http://repository.aeronomie.be>) with the identifier doi (tbd).

681 The TROPOMI HONO dataset used in this study is available from the corresponding author upon
682 request.

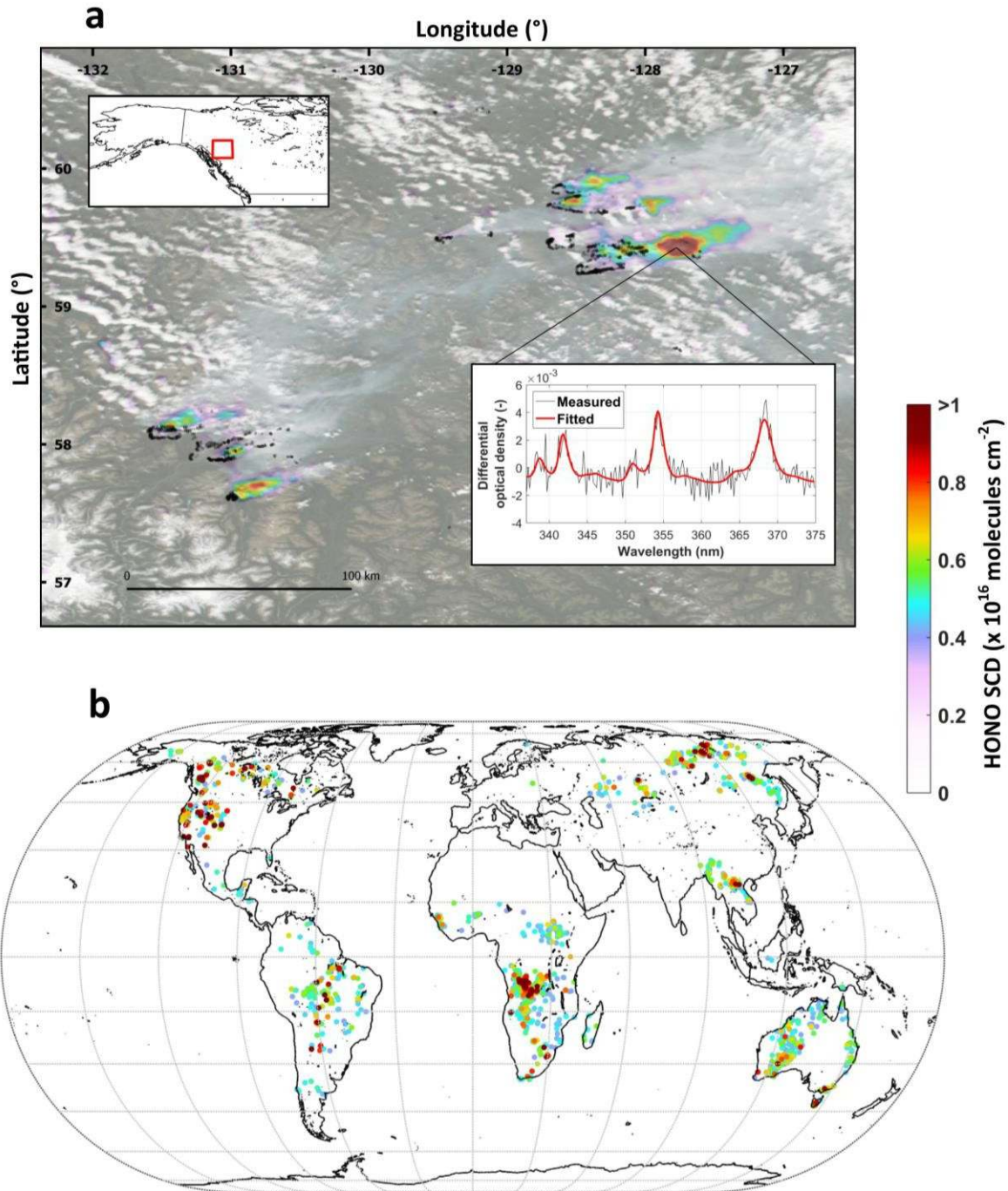
683 The BB-FLUX dataset is available on request and should be cited with the following reference:
684 Rainer Volkamer, Natalie Kille, Christopher F. Lee, Kyle J. Zarzana, Theodore K. Koenig, Benjamin
685 Howard, Christoph Knote, Teresa Campos, Larry Oolman, Dave Plummer, Min Deng, Zhien Wang,
686 Ravan Ahmadov, Brad Pierce, Florian Obersteiner, and Andreas Zahn, 2019; BB-FLUX: Biomass
687 Burning Fluxes of Trace Gases and Aerosols. University of Wyoming - Research Flight Center,
688 Laramie, WY. <http://flights.uwyo.edu/projects/bbflux18/>

689

690 **Code availability**

691 The DOAS code used to generate the satellite and aircraft data can be accessed at:[http://uv-
692 vis.aeronomie.be/software/QDOAS/index.php](http://uv-vis.aeronomie.be/software/QDOAS/index.php)

693 The chemical mechanism of the MAGRITTE model used in this study can be obtained at:
694 <https://tropo.aeronomie.be/index.php/models/magritte>



695

696 **Fig.1 | Detection of HONO in wildfire plumes by TROPOMI.** a, Example map of HONO slant
 697 column densities for wildfires in British Columbia on 21 August 2018. The background layer is a
 698 composite of true-color RGB image with fires detection and thermal anomalies product (black
 699 points) from VIIRS/Suomi-NPP instrument (source: <https://worldview.earthdata.nasa.gov/>),
 700 showing smoke aerosols and the fires source locations. The inset figure is the spectral proof of
 701 the HONO detection in the satellite pixel centered at 59.45°N, 127.82°W, illustrating the presence

702 of the HONO differential absorption in the measured spectrum. **b**, Global map of HONO SCD
703 detections (see Methods) for one year of TROPOMI measurements.

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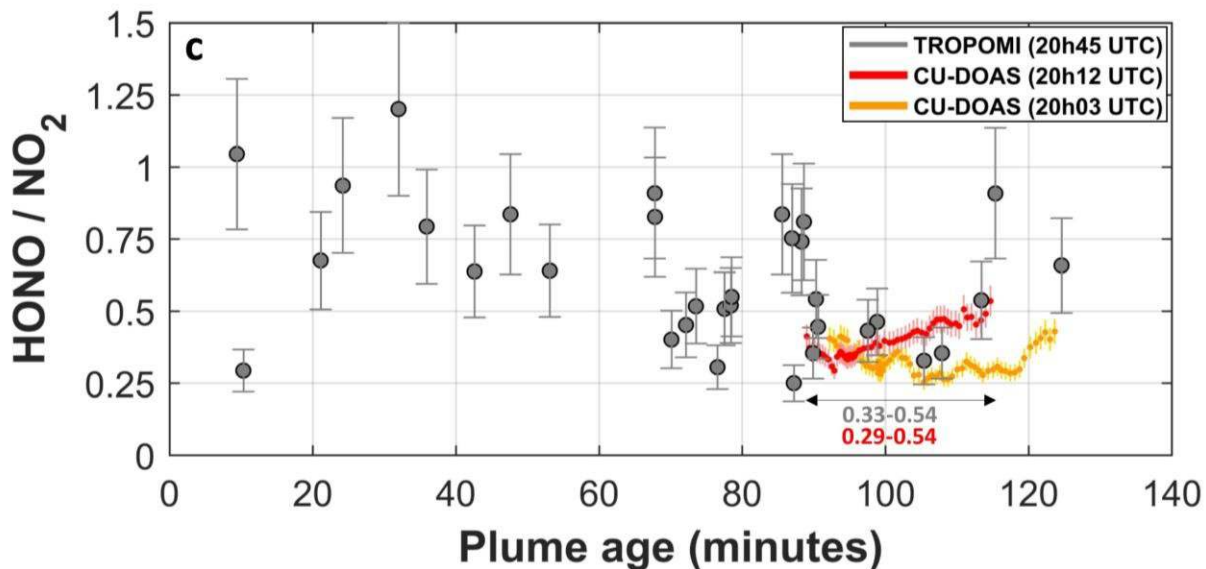
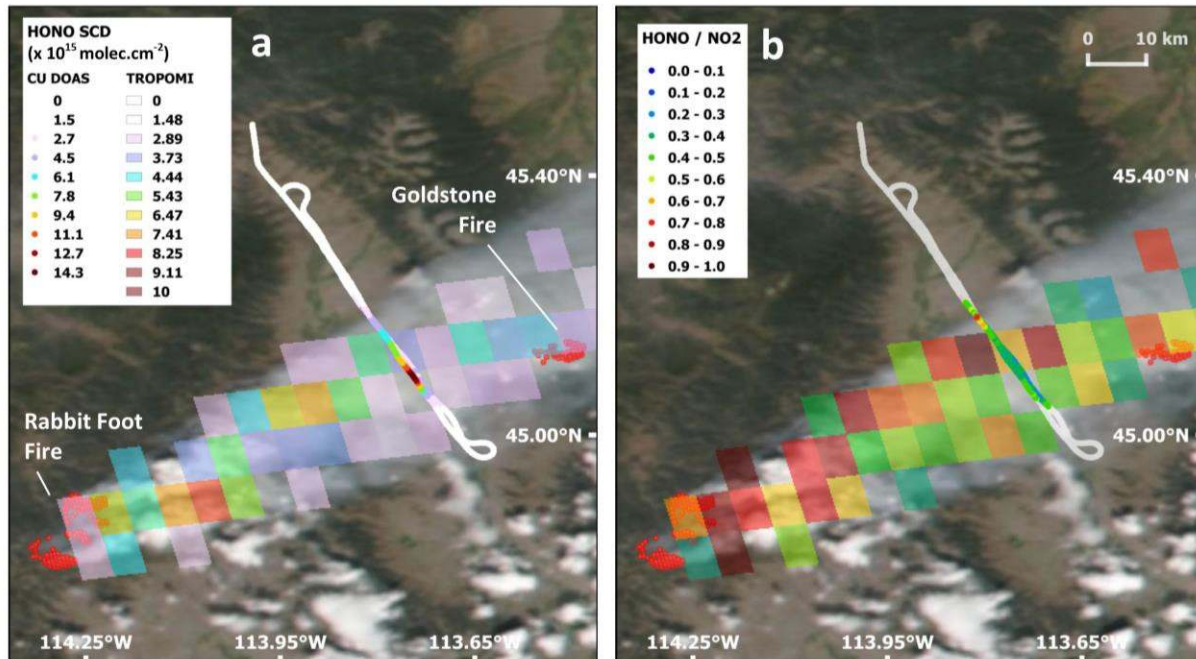
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711 **Fig. 2 | Comparison between TROPOMI and aircraft (CU-DOAS) measurements of the Rabbit**
 712 **Foot Fire (Idaho, USA) on August 12, 2018. a,** HONO slant columns from TROPOMI (rectangles)
 713 and aircraft CU-DOAS (dots). The color scales best represent the ranges of observed values. **b,**
 714 RHN for measurements with unambiguous detection of HONO and NO₂. The background image
 715 for (a-b) shows biomass burning aerosols and the fires source locations (same data source as Fig.
 716 1a). **c,** Comparison between TROPOMI and aircraft RHN as function of plume age (Methods). The
 717 two aircraft traverses of the plume are plotted separately. The ranges of RHN from TROPOMI and
 718 CU-DOAS are given over the intersection plume age interval (double arrow), for the traverse
 719 closest in time to the satellite. Error bars correspond to systematic uncertainties on RHNs.

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721 **Table 1.** RHNs reported in the literature (Supplementary Table S2) and in this study, for different
 722 types of biomass burning. The TROPOMI results are classified using MODIS land cover type³⁴.
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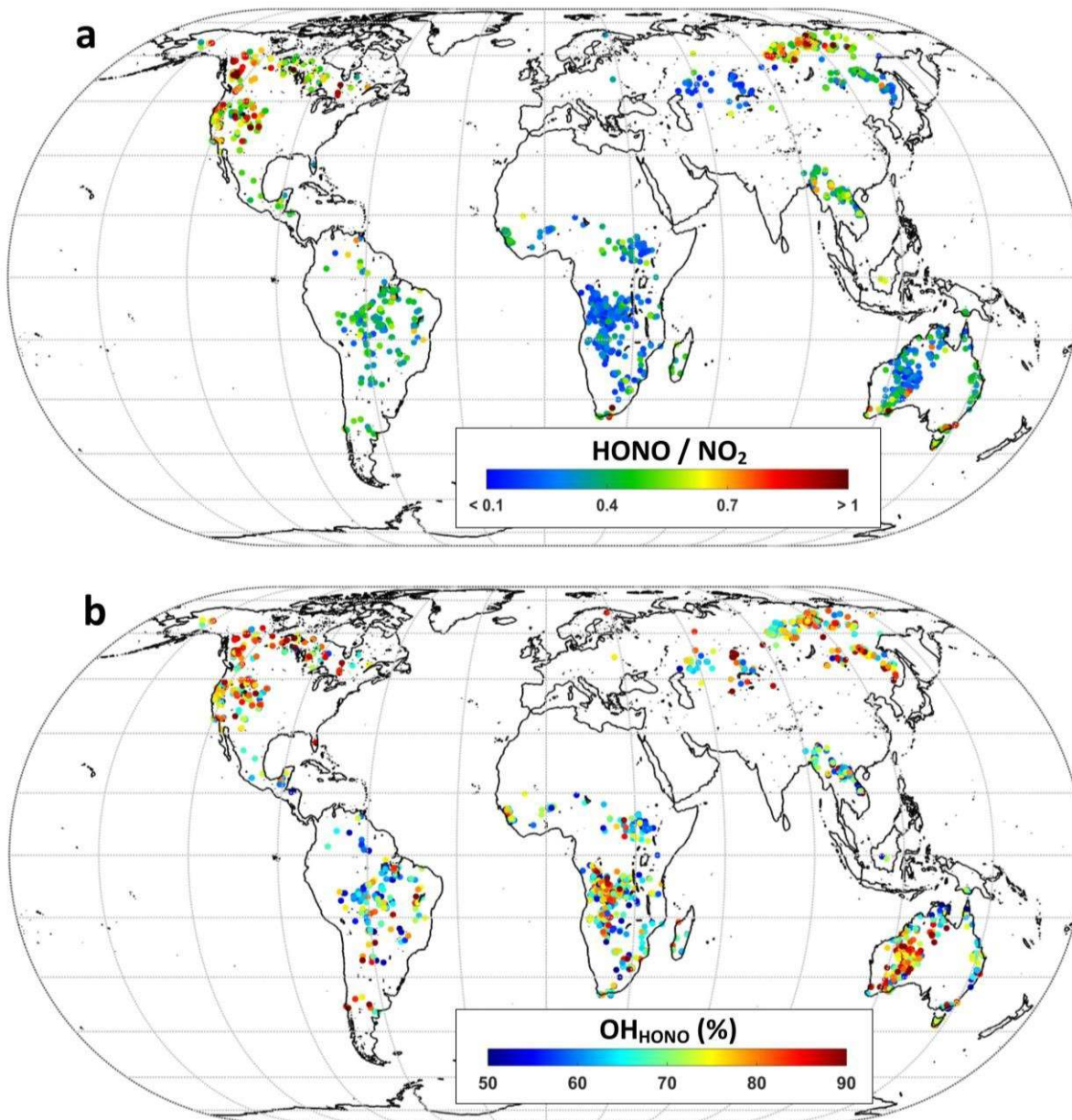
| | Savanna, grassland, shrubland | Tropical forest | Extra-tropical forest |
|-------------------------------|----------------------------------|------------------|----------------------------------|
| Field measurements | 0.05 – 0.10 | 0.17 – 0.22 | 0.06 – 0.41 (0.86 ^δ) |
| Laboratory experiments | 0.05 – 0.19 | 0.17 | 0.13 – 0.20 |
| This study*: average ± error* | 0.34±0.08 | 0.41±0.09 | 0.54±0.12 |

724 ^δ Fresh smoke from large wildfires³⁵.

725 * Mean values for satellite HONO detections, mostly representative of fires with carbon emissions of
 726 0.5 - 500 gC/m²/month (Supplementary Fig S2b).

727 ** Systematic uncertainty

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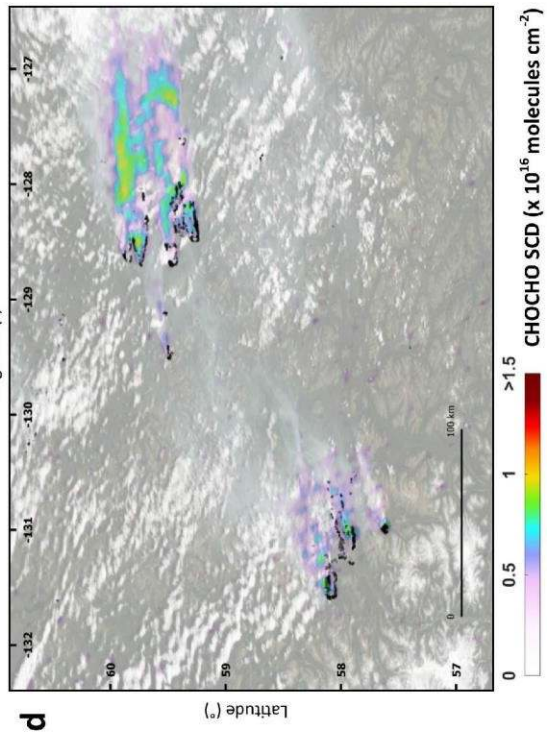
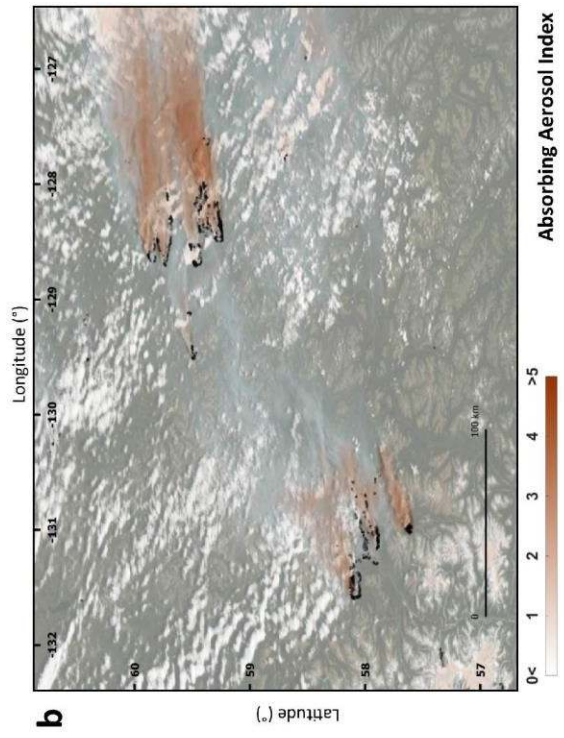
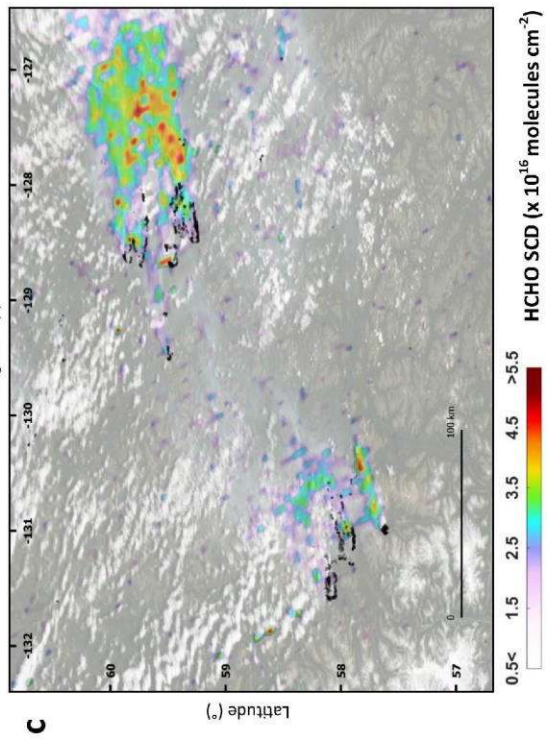
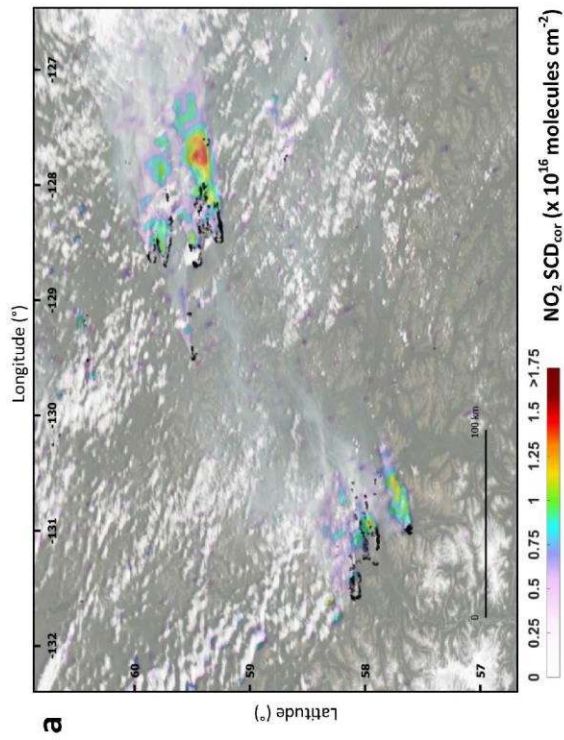
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730 **Fig. 3 | Satellite-derived RHN and relative production rate of OH due to HONO photolysis for**
 731 **fires emissions.** **a**, RHN for one year of TROPOMI measurements (May 2018 - April 2019). The
 732 coloured symbols correspond to individual HONO detections (same as Fig. 1b). **b**, Satellite
 733 estimates of OH production (in percent) from HONO fire emissions. The OH production is
 734 calculated from HONO concentrations derived from the satellite detections (as (a)), assuming a
 735 single air mass factor and a fixed HONO concentration profile shape (Methods).

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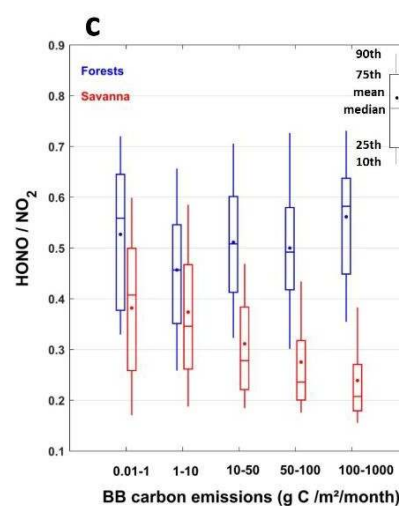
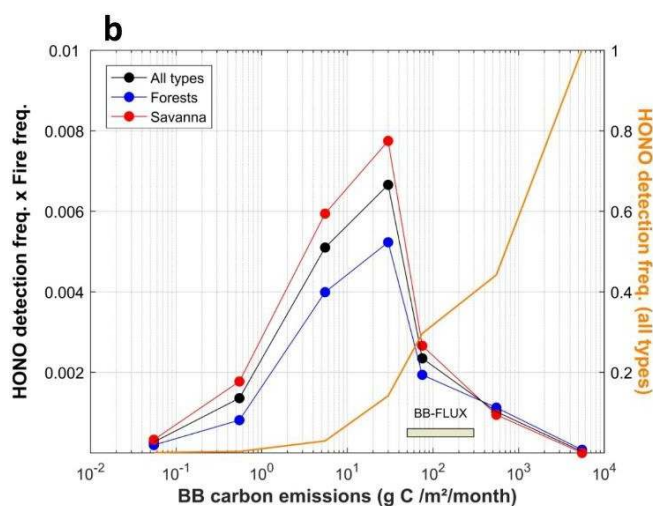
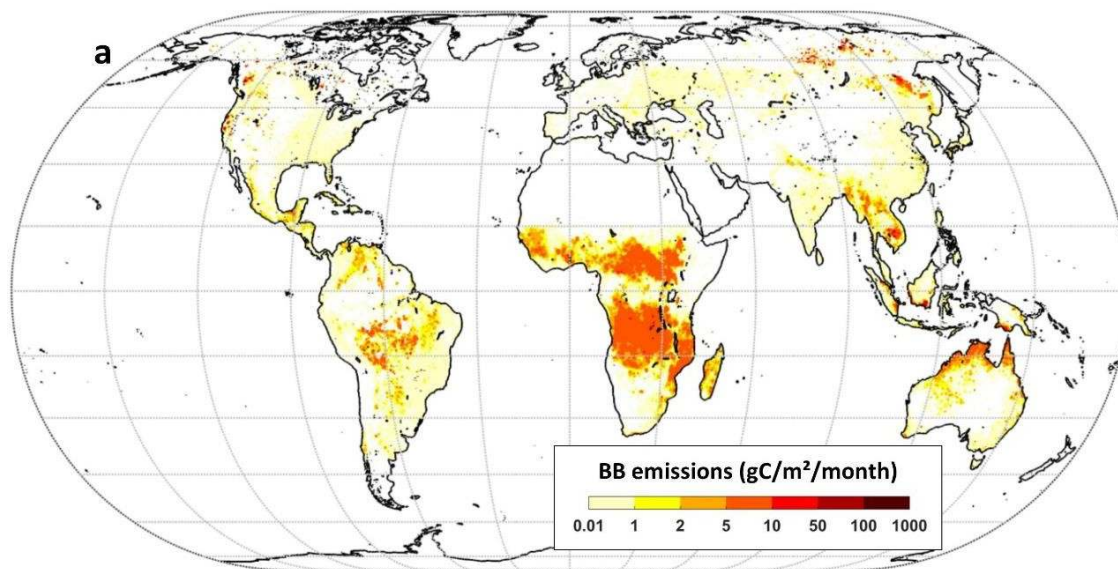
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738 **Supplementary Information contains Figures S1-S6, Tables S1-S8, two data files**
739 **in the form excel sheets for global compilation of HONO detections for one year**
740 **of TROPOMI measurements, and TROPOMI and aircraft data for the Rabbit Foot**
741 **fire validation case, and supplementary references.**



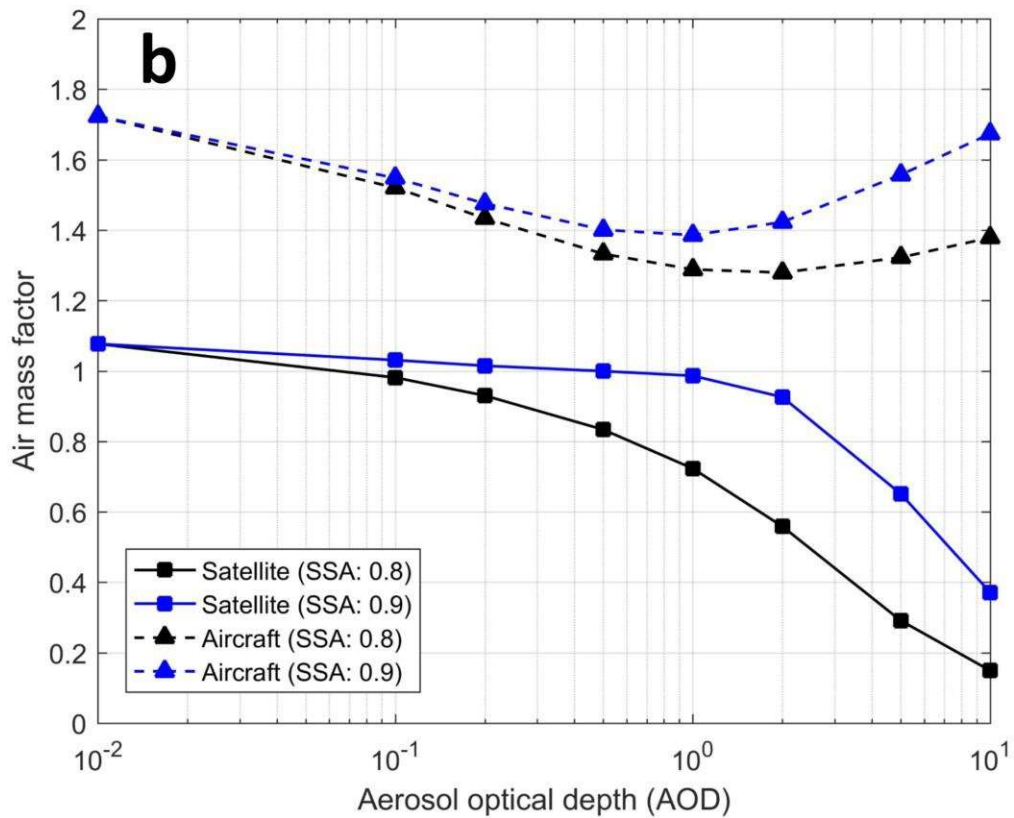
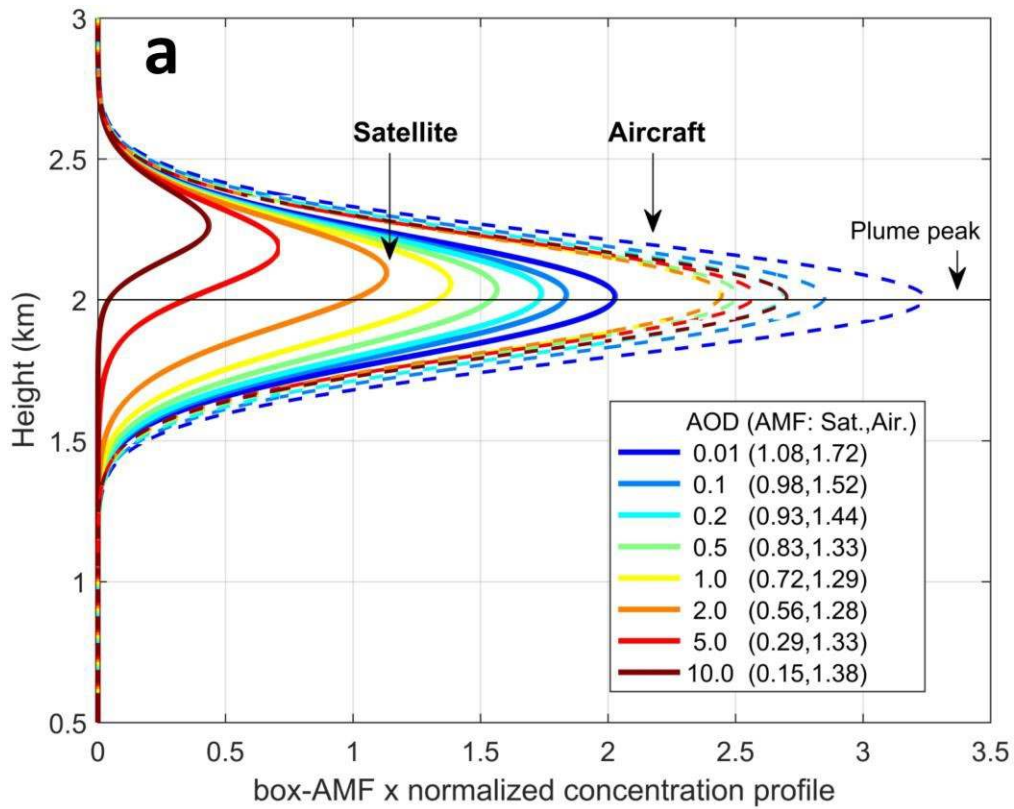
743 **Supplementary Fig. 1 | Examples of TROPOMI observations of nitrogen dioxide, absorbing**
744 **aerosol index, formaldehyde and glyoxal.** **a**, NO₂ slant column densities (corrected for
745 stratospheric NO₂ absorption), for British Columbia on 21 August 2018 (same as Fig. 1). NO₂ SCDs
746 are retrieved in the same wavelength interval as HONO SCDs. **b**, Absorbing aerosol index
747 (dimensionless) using the wavelength pair 354/388 nm. **c-d**, Formaldehyde and glyoxal slant
748 column densities, respectively. **b-d** are for the same scene as **(a)**. The background layers are true-
749 color RGB images with fires detection and thermal anomalies product (black points) from
750 VIIRS/Suomi-NPP instrument (source: <https://worldview.earthdata.nasa.gov/>), showing smoke
751 aerosols and the fires source locations.

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788 **Supplementary Fig. 2 | Global biomass burning carbon emissions, and statistical analysis of**
 789 **TROPOMI HONO detections and HONO/NO₂ with fire activity data.** **a**, Yearly averaged biomass
 790 burning carbon emissions from GFED (May 2018-April 2019). **b**, HONO detection frequency
 791 multiplied by fire frequency, per bin of carbon emission (monthly averages at 1°x1°), for savanna,
 792 forests and both biomes merged, based TROPOMI one-year measurements. HONO detections
 793 are mainly found for emissions of 0.5-500 g C/m²/month; small agriculture fires are not observed.
 794 The HONO detection frequency (in orange, for all vegetation types) is estimated, by the fraction
 795 of the grids with at least one HONO detection, for a particulate BB carbon emission rate. The pale
 796 yellow rectangle gives an indicative range of carbon emissions for the fires during the BB-FLUX
 797 campaign. **c**, Whisker plot of RHN for bins of carbon emissions (same as (b)), for savanna and
 798 forest fires.



800 **Supplementary Fig. 3 | Illustration of measurement sensitivity change for varying aerosol**
801 **optical depth for a smoke plume peaking at 2km. a,** Height-resolved contribution to the total
802 AMF (Methods) for satellite nadir and aircraft (at 1km flying altitude) zenith-sky viewing
803 geometries, as function of AOD. Satellite and aircraft total AMFs are in the legend. For the
804 satellite geometry, the reduction of sensitivity and shift towards the upper-part of the plume for
805 increasing AOD is clearly visible. Calculations are for clear-sky standard atmosphere, 30° solar
806 zenith angle, 0.05 surface albedo, and typical fresh biomass burning absorbing aerosols with
807 single scattering albedo (SSA) of 0.8. **b,** AMFs for satellite nadir and aircraft zenith-sky viewing
808 geometries, for the same conditions as (a), with SSA of 0.8-0.9.

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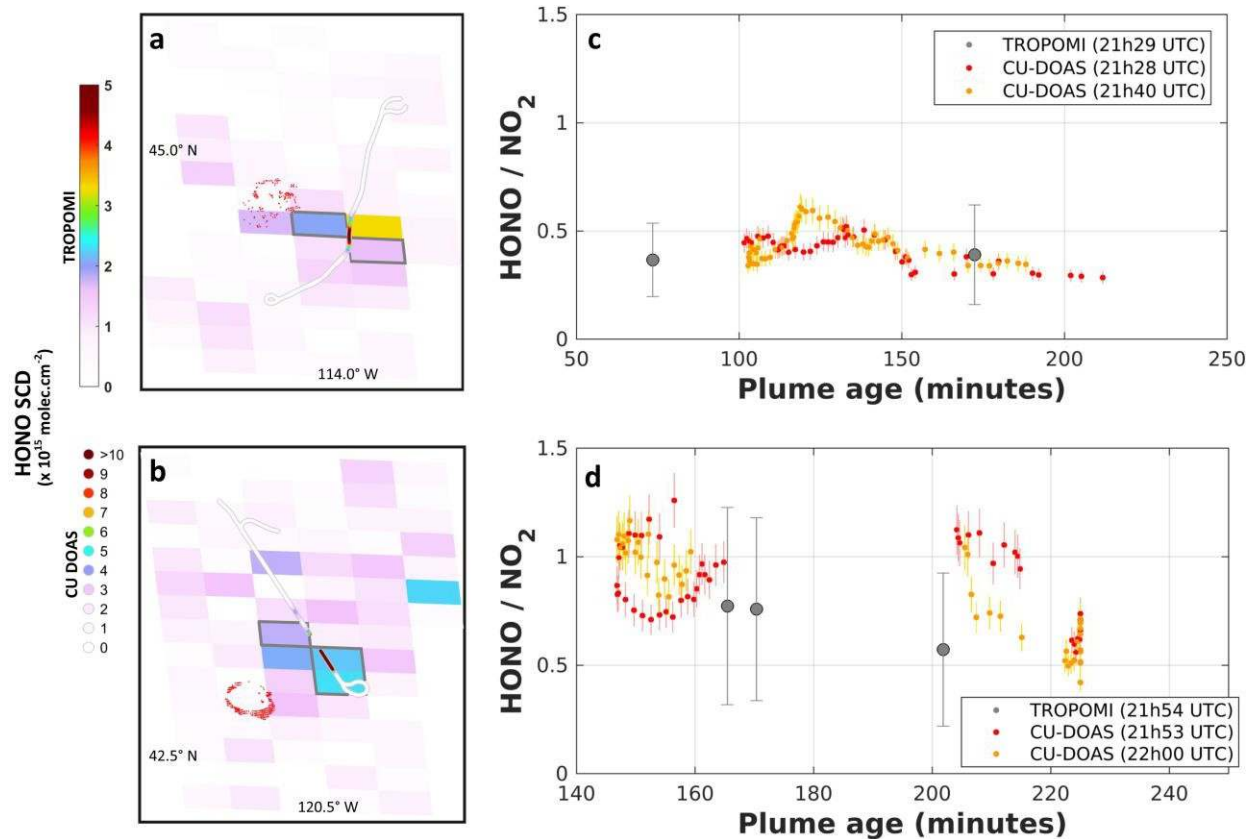
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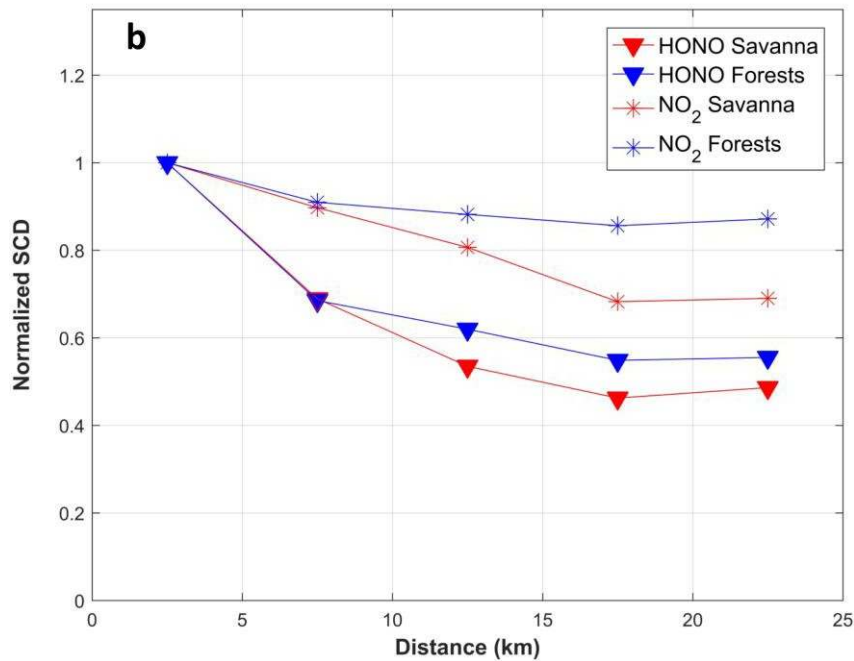
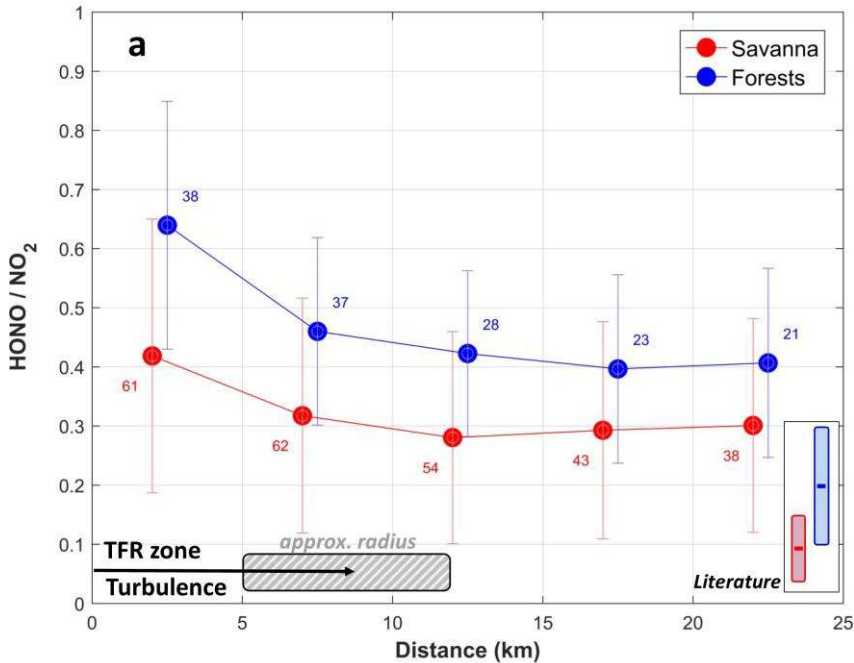
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 818 **Supplementary Fig. 4 | Comparison between TROPOMI and aircraft (CU DOAS) measurements**
 819 **of the Rabbit Foot (Idaho) and Watson Creek (Oregon) fires on August 15 and 19, 2018. a-b,**
 820 **HONO slant columns from TROPOMI (rectangles) and nearly synchronized (± 15 minutes)**
 821 **CU-DOAS (dots), for Rabbit Foot fire (a) and Watson Creek fire (b). The fires source locations are**
 822 **indicated by the red points (source: <https://firms.modaps.eosdis.nasa.gov/>).** **c-d, Comparison**
 823 **between TROPOMI and aircraft RHN as function of plume age (Methods), respectively for (a-b).**
 824 **TROPOMI pixels delineated by grey lines in (a-b) are used for the comparison, and correspond to**
 825 **unambiguous detections of both HONO and NO₂ with SCDs > 2x retrieval uncertainty (other pixels**
 826 **are considered not suitable for comparison). The two aircraft traverses of the plumes are plotted**
 827 **separately. Aircraft measurements more than 5 km away from the satellite pixels are not**
 828 **considered. Error bars correspond to systematic uncertainties on RHNs.**

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832 **Supplementary Fig. 5 | RHN and normalized slant columns dependence with distance from**
 833 **HONO maximum.** a, Averages of RHN for extra-tropical forest and savanna ecosystems, as a
 834 function of the distance from the measured HONO maxima for the 100 largest measured HONO
 835 SCDs. Error bars are RHN standard deviations; numbers are the total pixels per distance bin. RHN
 836 peaks are found within the 5-12 km radius of temporary flight restriction (TFR) zone or affected
 837 by fire-induced turbulence. The TROPOMI results are classified using MODIS land cover type¹.
 838 The inset colored bars indicate the range (mean \pm standard deviation) of RHN found in the

839 literature (Supplementary Table S2, excluding fresh plumes from large wildfires²). **b**, same as (a)
840 for the HONO and NO₂ slant column densities (normalized).

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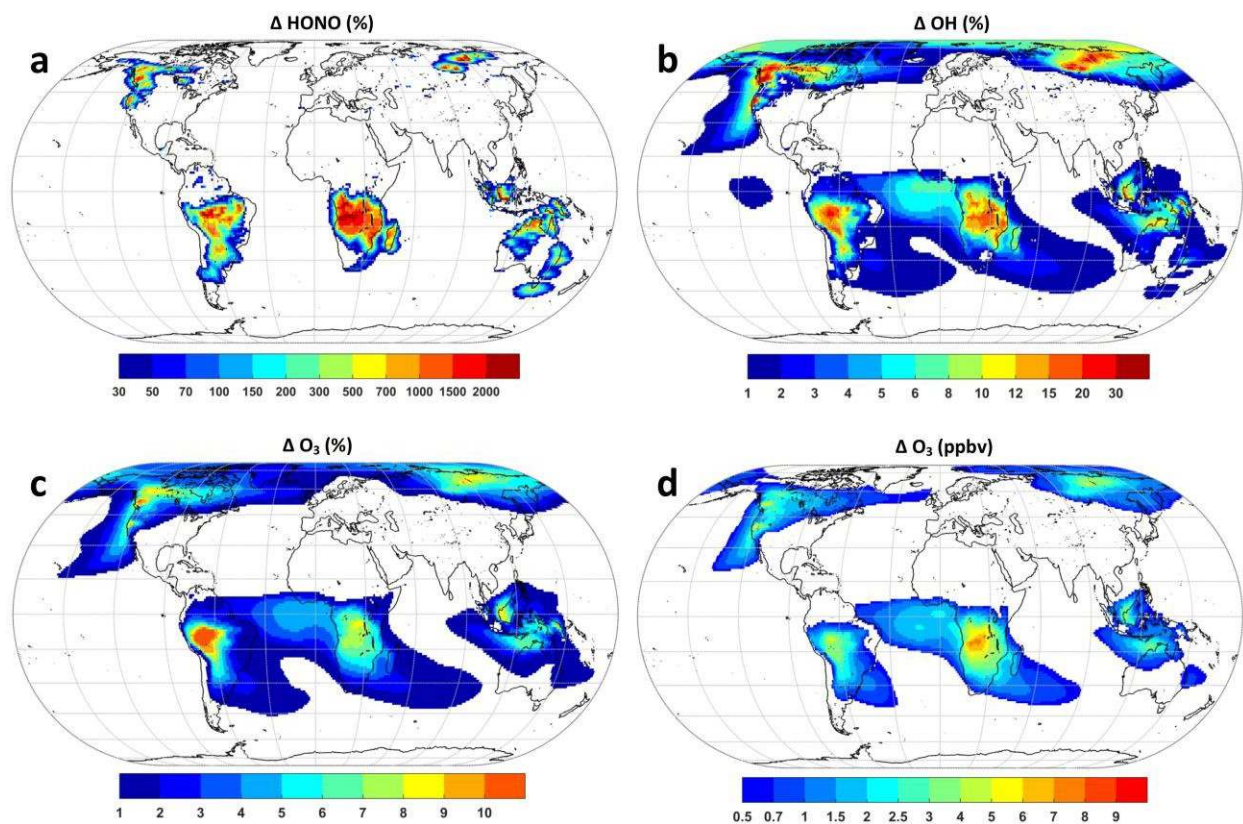
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 864 **Supplementary Fig. 6 | Modelled impact of pyrogenic HONO.** Calculated enhancement in the
 865 near-surface mixing ratios of HONO (a), OH (b) and O₃ (c-d) due to the inclusion of pyrogenic
 866 HONO emissions, for the month of August 2018.
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882 **Supplementary Table 1.** Summary error budget of NO₂ SCD, HONO SCD and RHN, for satellite and
 883 aircraft measurements* used in this study.

| | Satellite | Aircraft | Evaluation method - reference |
|--|----------------------|----------------------|---|
| NO₂ | | | |
| Random error (molec/cm ²) | 1.8x10 ¹⁵ | 0.6x10 ¹⁵ | Data scatter (1-σ) in clean regions |
| Random error (%) | 12 | 3 | |
| Absorption cross-section | | | |
| Uncertainty (%) | 3 | 3 | Vandaele et al. (1998) |
| Temperature [‡] dep. ± 20K (%) | 4 | ≤4 | Behrens et al. (2018) |
| Systematic error [§] (molec/cm ²) | 1.3x10 ¹⁵ | 0.9x10 ¹⁵ | Sensitivity tests |
| Systematic error (%) | 9 | 4 | |
| HONO | | | |
| Random error (molec/cm ²) | 0.7x10 ¹⁵ | 0.2x10 ¹⁵ | Data scatter (1-σ) in clean regions |
| Random error (%) | 9 | 2 | |
| Absorption cross-section (%) | 6 | 6 | Stutz et al. (2000), Gratien et al. (2009) |
| Systematic error [§] (molec/cm ²) | 0.8x10 ¹⁵ | 0.3x10 ¹⁵ | Sensitivity tests |
| Systematic error (%) | 11 | 3 | |
| RHN | | | |
| Random error ** (%) | 21.2 (40) | 5.1 | Precision of single measurement |
| Systematic error ** (%) | 26.7 (25) | 10.0 | Accuracy for comparison with literature |
| AMF cancellation (%) | 1 | 0.2 | AMF calculations over DOAS fit interval ^δ |
| Comparison total error (%) | 25.5 | 6.9 | Accuracy excluding cross-sections errors |
| Mean relative difference (%) (satellite – aircraft) ± statistical error | +6 ± 8 | | Figure 2c and Supplementary Figure S4 over plume age intersection |

884 * SCD percent errors given for typical HONO SCDs of 0.75 and 1.0 x10¹⁶ molec/cm², NO₂ SCDs of 1.5 and 2.25 x10¹⁶
 885 molec/cm², for satellite and aircraft observations, respectively.

886 ** Satellite RHN errors vary depending on the observation conditions and retrieved SCDs of HONO and NO₂. An
 887 upper limit RHN random error is of 40% for low SCDs. A global estimate of RHN systematic error is of about 25%
 888 when accounting for the range of observed SCDs including the conditions with high NO₂ (savanna fires).

889 ^δ Radiative transfer simulations for varying aerosol optical depth and single scattering albedo (as in Supplementary
 890 Fig. S3). Vertical profile shapes of HONO and NO₂ taken identical.

891 [‡] Difference between plume mean temperature and 294K used in DOAS spectral fitting. The effective plume
 892 temperature of the Rabbit Foot fire plume was 277 ± 2 K, and the <4% error is an upper limit.

893 [§] Mean values derived by varying the settings of the DOAS analysis and SCD background corrections.

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895 **Supplementary Table 2.** RHNs reported in the literature and in this study, for different types of
 896 biomass burning. For each literature study, the results are given as means. The TROPOMI results
 897 are classified using MODIS land cover type¹.

| | Savanna, grassland, shrubland | Tropical forest | Extra-tropical forest |
|--|----------------------------------|--------------------|---------------------------------------|
| Field measurements | 0.05 – 0.10 | 0.17 – 0.22 | 0.06 – 0.41 (0.86^δ) |
| Trentman et al. (2005) | 0.05 | - | - |
| Burling et al. (2011) | 0.10 | - | 0.14 |
| | (oak savanna) | | |
| Akagi et al. (2012) | - | - | 0.17 |
| | | | (chaparral) |
| Akagi et al. (2013) | - | - | 0.27 |
| Bytnerowicz et al. (2016) | - | - | 0.06 |
| Müller et al. (2016) | - | - | 0.21 |
| Weise et al. (2015) | - | - | 0.19 |
| Yokelson et al. (2007) | - | 0.17 | - |
| Yokelson et al. (2009) | - | 0.22 | - |
| Yokelson et al. (2013) | - | - | 0.41 |
| | | | (coniferous canopy) |
| Peng et al. (2020) | - | - | 0.86 |
| Laboratory experiments[§] | 0.05 – 0.19 | 0.17 | 0.13 – 0.20 |
| Burling et al. (2010) | 0.05 | - | 0.13 |
| Keene et al. (2006) | - | 0.17 | - |
| Selimovic et al. (2018) | - | - | 0.19 |
| Stockwell et al. (2015) | 0.07 | - | 0.20 |
| Yokelson et al. (2013) | 0.19 | - | - |
| | (semiarid shrubland) | | |
| This study: average ± error* | 0.34±0.08 | 0.41±0.09 | 0.54±0.12 |
| (10 th - 90 th percentile) | (0.14 - 0.61) | (0.23 - 0.62) | (0.32 - 0.78) |

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899 ^δ Fresh smoke from large wildfires.

900 [§] NO₂ is assumed in a non-photostationary state for control burns. HONO/NO₂ values are calculated for 901 HONO/NO_x molar emission ratios, adapted from reported emission factors (g kg⁻¹ of dry matter) of HONO 902 and NO_x (as NO). A fixed NO_x/NO₂ ratio of 1.2 is applied to estimate HONO/NO₂ ratios representative of 903 atmospheric measurements of biomass burning plumes²¹.

904 * Systematic uncertainty

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928 **Supplementary Table 3.** DOAS settings used in this study for TROPOMI retrievals of HONO, NO₂,
 929 HCHO and CHOCHO.
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| HONO and NO₂ | |
|--------------------------------|--|
| Fitting interval | 337-375 nm (TROPOMI band 3) |
| Cross-sections | HONO 296K (Stutz et al., 2010), NO ₂ 294K (Vandaele et al., 1998), water vapor (Polyansky et al., 2018), O ₂ -O ₂ 293K (Thalman and Volkamer, 2013), O ₃ 223K and 243K (Serdyuchenko et al., 2014), BrO 223K (Fleischmann et al., 2004), HCHO 298K (Meller and Moortgat, 2000), Ring (Chance and Spurr, 1997) |
| Polynomial | 5 th order |
| Intensity offset | Linear, 1 st order |
| Wavelength shift | 1 st order |
| Reference spectrum | Daily radiance (averaged per across-track position) in equatorial Pacific sector (150°E-110°W, 5°S-5°N) |
| Post-processing | NO ₂ SCD stratospheric correction: Latitudinal parameterization (per across-track position) in clean Pacific sector (160°E-150°W) |
| HCHO | |
| Fitting interval | 328.5-359 nm (TROPOMI band 3) |
| Cross-sections | HCHO 298K (Meller and Moortgat, 2000), NO ₂ 220K (Vandaele et al., 1998), O ₂ -O ₂ 293K (Thalman and Volkamer, 2013), BrO 223K (Fleischmann et al., 2004), Ring (Chance and Spurr, 1997), O ₃ 223K and 243K (Serdyuchenko et al., 2014) + Non-linear O ₃ absorption effect: 2 pseudo-cross sections from the Taylor expansion of the wavelength and the O ₃ optical depth (Puķīte et al., 2010). |
| Polynomial | 5 th order |
| Intensity offset | Linear, 1 st order |
| Wavelength shift | 1 st order |
| Reference spectrum | Daily radiance (averaged per across-track position) in equatorial Pacific sector (150°E-110°W, 5°S-5°N) |
| CHOCHO | |
| Fitting interval | 435-460 nm (TROPOMI band 4) |

| | |
|---------------------------|---|
| Cross-sections | CHOCHO (Volkamer et al., 2005), NO ₂ 220K and 294K (Vandaele et al., 1998), water vapor (Rothman et al., 2013), O ₂ -O ₂ 293K (Thalman and Volkamer, 2013), O ₃ 243K (Serdyuchenko et al., 2014), H ₂ O liquid (Mason et al., 2016), Ring (Chance and Spurr, 1997) |
| Polynomial | 3 rd order |
| Intensity offset | Linear, 1 st order |
| Wavelength shift | 1 st order |
| Reference spectrum | Daily radiance (averaged per across-track position) in equatorial Pacific sector (180°E-120°W, 15°S-15°N) |

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952 **Supplementary Table S4.** VOC photolysis reactions considered as radical sources; OH yield Y_{OH}
 953 (assuming $NO/NO_2 = 0.2$ in biomass burning plumes); ratio of their photolysis rates (radical
 954 channel only) relative to that of HCHO, calculated at 30° zenith angle for 300 DU ozone; and
 955 relative uncertainty (%) on the product $Y_{OH} \times J_{VOC}$, accounting for uncertainties on the photolysis
 956 parameters, based on compilations of experimental data from JPL³² and IUPAC³³, and on the yield
 957 of OH, assuming a 50% error in the conversion of acylperoxy radicals into OH radicals (resulting
 958 from a factor of 2 error in the NO to NO_2 ratio).

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| Reactions | $Y_{OH}(VOC)$ | J_{VOC}/J_{HCHO} ($s^{-1}s$) | $\sigma(Y_{OH} \times J_{VOC})$ (%) |
|--|---------------|-------------------------------------|--|
| HCHO \rightarrow H+HCO | 2 | 1.00 | 15 |
| CH ₃ CHO \rightarrow CH ₃ +CHO | 2 | 0.146 | 15 |
| C ₂ H ₅ CHO \rightarrow C ₂ H ₅ +CHO | 2 | 0.232 | 20 |
| C ₃ H ₇ CHO \rightarrow C ₃ H ₇ +CHO | 2 | 1.094 | 30 |
| CH ₃ COCH ₃ \rightarrow CH ₃ CO+CH ₃ | 1.3 | 0.0162 | 27 |
| C ₂ H ₅ COCH ₃ \rightarrow CH ₃ CO+C ₂ H ₅ | 1.3 | 0.080 | 60 |
| acrolein \rightarrow products | 0.39 | 0.030 | 30 |
| crotonaldehyde \rightarrow products | 2 | 0.042 | 30 |
| methacrolein \rightarrow products | 1.51 | 0.061 | 100 |
| methylvinylketone \rightarrow CH ₃ CO+CH ₂ =CH | 1.3 | 0.066 | 60 |
| HOCH ₂ CHO \rightarrow CHO+CH ₂ OH | 2 | 0.346 | 30 |
| HOCH ₂ COCH ₃ \rightarrow CH ₃ CO+CH ₂ OH | 1.3 | 0.056 | 50 |
| CHOCHO \rightarrow 2 CHO | 2 | 2.23 | 60 |
| CH ₃ COCHO \rightarrow CH ₃ CO+CHO | 1.3 | 4.13 | 60 |
| CH ₃ COCOCH ₃ \rightarrow 2 CH ₃ CO | 0.6 | 8.42 | 100 |
| 2-furfural \rightarrow products | 2 | 0.23 | 100 |

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962 **Supplementary Table S5.** Alkene ozonolysis reactions considered as radical sources; OH yield;
 963 reaction rate constant at 286 K; OH production for 1 ppbv VOC at 286 K, with 50 ppbv O₃ and
 964 [M]=1.9×10¹⁹ molec. cm⁻³, calculated as $P_{OH}(VOC+O_3, \text{ in pptv h}^{-1}) = k(VOC+O_3) \times [O_3 \text{ in molec. cm}^{-3}] \times (\text{OH yield}) \times 3600 \times 10^3$;
 965 and relative uncertainty (%) on OH production, accounting for
 966 uncertainties in the OH yield (assumed equal to 20%) and in the reaction rate constant³⁴. OH
 967 production from monoterpenes + O₃ depends on speciation (see text). The large uncertainty for
 968 monoterpenes $\sigma(P_{OH}(VOC+O_3))$ allows for a factor of 3 error on α - to β -pinene ratio in fire plumes.

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| Reactions | OH yield | $k(VOC+O_3)$ (10 ⁻¹⁸ molec. ⁻¹ cm ³ s ⁻¹) | $P_{OH}(VOC+O_3)$ (pptv h ⁻¹) | $\sigma(P_{OH}(VOC+O_3))$ (%) |
|------------------------------------|----------|---|--|----------------------------------|
| ethene + O ₃ | 0.26 | 1.1 | 1 | 45 |
| propene + O ₃ | 0.92 | 7.7 | 24 | 55 |
| 1-butene + O ₃ | 0.92 | 8.0 | 25 | 40 |
| i-butene + O ₃ | 1.64 | 9.0 | 50 | 35 |
| trans-2-butene + O ₃ | 1.39 | 160 | 758 | 45 |
| cis-2-butene + O ₃ | 1.39 | 110 | 521 | 45 |
| butadiene + O ₃ | 0.29 | 4.6 | 46 | 55 |
| 1-pentene + O ₃ | 0.92 | 10 | 31 | 55 |
| 1-hexene + O ₃ | 0.92 | 11 | 34 | 55 |
| isoprene + O ₃ | 0.56 | 9.6 | 18 | 35 |
| α -pinene + O ₃ | 1.60 | 86 | 469 | 55 |
| β -pinene + O ₃ | 0.70 | 16 | 38 | 55 |
| monoterpenes + O ₃ | | | 146 | 200 |

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975 **Supplementary Table 6.** Molar enhancement ratios in biomass burning plumes relative to
 976 HCHO³⁵. The standard error is given between parentheses, accounting for the standard deviation
 977 and number of measurements for each VOC. Those errors might be overestimated given the
 978 expected (but not quantified) correlation between $\Delta(\text{VOC})$ and $\Delta(\text{HCHO})$.

| | $\Delta(\text{VOC})/\Delta(\text{HCHO})$ (mol/mol) | | | |
|---|--|------------------|-------------------|----------------|
| | savanna | tropical forests | temperate forests | boreal forests |
| CH ₃ CHO | 0.488(0.126) | 0.673(0.476) | 0.367(0.059) | 0.316(0.045) |
| C ₂ H ₅ CHO | 0.022(0.016) | 0.022(0.022) | 0.022(0.005) | 0.071(0.071) |
| C ₃ H ₇ CHO | 0.037(0.033) | 0.023(0.016) | 0.022(0.006) | 0.038(0.038) |
| CH ₃ COCH ₃ | 0.198(0.029) | 0.136(0.136) | 0.144(0.031) | 0.470(0.183) |
| C ₂ H ₅ COCH ₃ | 0.044(0.014) | 0.087(0.087) | 0.046(0.014) | 0.032(0.00) |
| acrolein | 0.209(0.044) | 0.145(0.145) | 0.088(0.033) | 0.101(0.101) |
| crotonaldehyde | 0.087(0.087) | 0.043(0.043) | 0.082(0.082) | 0.105(0.105) |
| methacrolein | 0.045(0.045) | 0.025(0.025) | 0.027(0.016) | 0.024(0.015) |
| methylvinylketone | 0.080(0.080) | 0.070(0.070) | 0.034(0.010) | 0.024(0.017) |
| HOCH ₂ CHO | 0.088(0.034) | 0.091(0.091) | 0.097(0.097) | 0.137(0.137) |
| HOCH ₂ COCH ₃ | 0.185(0.057) | 0.230(0.230) | 0.220(0.220) | 0.161(0.161) |
| CHOCHO | 0.168(0.168) | 0.129(0.129) | 0.162(0.162) | 0.204(0.204) |
| CH ₃ COCHO | 0.136(0.096) | 0.090(0.090) | 0.054(0.054) | 0.145(0.145) |
| CH ₃ COCOCH ₃ | 0.099(0.028) | 0.106(0.106) | 0.149(0.064) | 0.068(0.068) |
| 2-Furfural | 0.185(0.108) | 0.102(0.102) | 0.078(0.046) | 0.109(0.109) |
| Ethane | 0.740(0.066) | 0.496(0.048) | 0.577(0.035) | 0.943(0.153) |
| propene | 0.267(0.051) | 0.256(0.213) | 0.216(0.146) | 0.273(0.254) |
| 1-butene | 0.036(0.006) | 0.016(0.011) | 0.031(0.005) | 0.049(0.022) |
| i-butene | 0.018(0.003) | 0.024(0.024) | 0.022(0.006) | 0.016(0.006) |
| trans-2-butene | 0.009(0.002) | 0.007(0.005) | 0.010(0.003) | 0.009(0.003) |
| cis-2-butene | 0.007(0.001) | 0.007(0.005) | 0.010(0.003) | 0.007(0.003) |

| | | | | |
|--------------|--------------|--------------|--------------|--------------|
| butadiene | 0.043(0.007) | 0.035(0.035) | 0.033(0.005) | 0.028(0.005) |
| 1-pentene | 0.008(0.001) | 0.010(0.010) | 0.010(0.002) | 0.011(0.003) |
| 1-hexene | 0.012(0.002) | 0.010(0.010) | 0.014(0.002) | 0.022(0.022) |
| isoprene | 0.036(0.018) | 0.040(0.028) | 0.021(0.00) | 0.019(0.019) |
| monoterpenes | 0.019(0.008) | 0.014(0.014) | 0.124(0.069) | 0.139(0.139) |

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998 **Supplementary Table 7.** Contribution of VOC photolysis reactions to the production of OH
 999 radicals, relative to that of HCHO, based on the yields and rates of Supplementary Table 4 and on
 1000 the enhancement ratios of Supplementary Table 6. The estimated uncertainty is given within
 1001 parentheses.

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| | $P_{OH}(VOC)/P_{OH}(HCHO)$ (pptv h ⁻¹ pptv ⁻¹ h) | | | |
|---|--|------------------|-------------------|----------------|
| | savanna | tropical forests | temperate forests | boreal forests |
| CH ₃ CHO | 0.071(0.029) | 0.098(0.084) | 0.054(0.017) | 0.046(0.013) |
| C ₂ H ₅ CHO | 0.005(0.005) | 0.005(0.006) | 0.005(0.002) | 0.016(0.019) |
| C ₃ H ₇ CHO | 0.040(0.048) | 0.025(0.025) | 0.024(0.014) | 0.042(0.055) |
| CH ₃ COCH ₃ | 0.002(0.001) | 0.001(0.001) | 0.001(0.001) | 0.004(0.003) |
| C ₂ H ₅ COCH ₃ | 0.002(0.002) | 0.004(0.006) | 0.002(0.002) | 0.002(0.001) |
| acrolein | 0.001(0.001) | 0.001(0.001) | 0.001(0.001) | 0.001(0.001) |
| crotonaldehyde | 0.004(0.005) | 0.002(0.003) | 0.003(0.004) | 0.004(0.005) |
| methacrolein | 0.002(0.004) | 0.001(0.002) | 0.001(0.002) | 0.001(0.002) |
| methylvinylketone | 0.003(0.005) | 0.003(0.005) | 0.001(0.001) | 0.001(0.001) |
| HOCH ₂ CHO | 0.030(0.021) | 0.031(0.040) | 0.034(0.044) | 0.047(0.061) |
| HOCH ₂ COCH ₃ | 0.007(0.006) | 0.008(0.012) | 0.008(0.012) | 0.006(0.009) |
| CHOCHO | 0.375(0.600) | 0.288(0.461) | 0.361(0.578) | 0.455(0.728) |
| CH ₃ COCHO | 0.365(0.32) | 0.242(0.387) | 0.145(0.232) | 0.389(0.622) |
| CH ₃ COCOCH ₃ | 0.250(0.321) | 0.268(0.536) | 0.376(0.538) | 0.172(0.344) |
| 2-Furfural | 0.043(0.068) | 0.023(0.046) | 0.018(0.029) | 0.025(0.050) |
| ALL except CHOCHO | 0.825(0.48) | 0.71(0.67) | 0.67(0.59) | 0.76(0.72) |

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1005 **Supplementary Table 8.** Contribution of VOC ozonolysis reactions to the production of OH
 1006 radicals calculated for 50 ppbv O₃ at 286 K, based on the molar enhancement ratios of
 1007 Supplementary Table 6, for 1 ppbv HCHO and [M]=1.9 10¹⁹ molec. cm⁻³. The uncertainties
 1008 (accounting for uncertainties in ozonolysis rates and yields, and in the molar enhancements in
 1009 fire plumes) are given within parentheses.

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| | P_{OH}(VOC) (pptv h⁻¹) | | | |
|----------------|--|-------------------------|--------------------------|-----------------------|
| | savanna | tropical forests | temperate forests | boreal forests |
| ethene | 0.72(0.39) | 0.49(0.27) | 0.57(0.29) | 0.93(0.57) |
| propene | 6.44(.77) | 6.18(8.54) | 5.21(6.39) | 6.59(9.76) |
| 1-butene | 0.91(0.52) | 0.40(0.44) | 0.78(0.44) | 1.23(1.04) |
| i-butene | 0.45(0.03) | 0.61(0.82) | 0.55(0.3) | 0.40(0.29) |
| trans-2-butene | 6.82(4.58) | 5.31(6.18) | 7.58(5.69) | 6.82(5.34) |
| cis-2-butene | 3.66(2.17) | 3.66(4.26) | 5.21(3.91) | 3.66(3.22) |
| butadiene | 1.95(1.39) | 1.59(2.46) | 1.50(1.05) | 1.27(0.93) |
| 1-pentene | 0.36(0.24) | 0.45(0.70) | 0.45(0.34) | 0.49(0.40) |
| 1-hexene | 0.28(0.20) | 0.34(0.53) | 0.49(0.34) | 0.76(1.18) |
| isoprene | 0.66(0.69) | 0.74(0.93) | 0.38(0.28) | 0.34(0.53) |
| monoterpenes | 2.80(6.78) | 2.05(6.15) | 18.1(46.2) | 20.3(60.9) |
| ALL | 25.1(9.9) | 21.8(13.3) | 40.8(47.2) | 42.8(62.1) |

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