

1 **24-hour evolution of an exceptional HONO plume emitted by the record-breaking**
2 **2019/2020 Australian Wildfire tracked from space: role of heterogeneous**
3 **photoinduced production**
4

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12 **Key Points:**

- 13 • Tracking HONO fire plumes at free tropospheric levels by IR sounders
14 • Persistent HONO concentrations observed at sunrise
15 • Importance of primary fire emissions and heterogeneous photo-induced reaction for
16 modelling the HONO plume
17

18 **Abstract**

19 Mega-fires have occurred in Australia during the 2019/2020 bushfire season, leading to enhanced
20 concentrations of many tropospheric pollutants. Here we report on a fire plume with unusually
21 high and persistent HONO levels that we could track during one day at free tropospheric levels
22 over the Tasman Sea on 4 January 2020 using IASI and CrIS satellite observations. HONO
23 concentrations up to about 8 ppb were retrieved during nighttime. Persistent HONO concentrations
24 (>1ppb) were still observed at sunrise. Model simulations suggest a significant contribution of
25 primary fire emissions and heterogeneous photo-induced reactions to explain the observed
26 concentrations. However, many uncertainties and unknowns remain in the plume aerosol load and
27 in the chemical processes which may explain the model inability to reproduce HONO
28 concentrations at sunrise.

29 **Plain Language Summary**

30 Mega-fires have occurred in Australia during the 2019/2020 bushfire season, called the Australian
31 Black Summer. They led to enhanced concentrations of many tropospheric pollutants in the
32 Southern Hemisphere. Amongst them, HONO plays a key role for oxidative capacity of the
33 atmosphere. An exceptional HONO plume with concentrations up to 8 ppb, has been tracked
34 during one day between 5 and 15 km over the Tasman Sea on 4 January 2020 by satellite
35 instruments. If HONO nighttime production is well known, persistence of high HONO
36 concentrations at sunrise one day after the emissions is unusual. Model simulations suggest a
37 significant contribution of primary fire emissions and heterogeneous photo-induced reactions to
38 explain the observed concentrations. However, many unknowns remain in the plume aerosol load
39 and in the chemistry which may explain the model inability to reproduce HONO concentrations at
40 sunrise.

41 **1 Introduction**

42 Nitrous acid (HONO) is one of the primary sources of hydroxyl radicals (OH) by photolysis
43 and then plays a key role in tropospheric chemistry for the oxidative capacity of the atmosphere
44 (Finlayson-Pitts & Pitts, 1999). Primary emissions of HONO in the atmosphere are from
45 combustion (e.g. Aumont et al., 2003) and soils (Stemmler et al., 2006). Its secondary production
46 proceeds through the gas phase reaction of NO and OH and by reactions of nitrogen-containing
47 compounds and especially NO₂ on surfaces or on aerosols (Aumont et al., 2003; Finlayson-Pitts
48 & Pitts, 1999). Rapid photolysis during daytime is the main HONO sink and leads to a short
49 lifetime in the order of tenths of minutes around local noon, which limits HONO concentrations
50 during daytime. However, large daytime HONO concentrations have already been reported by
51 several studies pointing at unknown or not well quantified sources, such as photo-induced
52 heterogeneous formation (e.g. Kleffmann, 2007; Lu et al., 2018; Neuman et al., 2016). At night,
53 without fast photo-dissociation, HONO tends to accumulate in the atmosphere to light-independent
54 heterogeneous formation on surfaces. The HONO distribution throughout the troposphere is not
55 well known (e.g. J. Kleffmann & Wiesen, 2008) compared to the near surface. Wildfires can have
56 a significant impact on HONO concentrations in the troposphere. Aircraft and ground based
57 measurements have been made but mainly in the planetary boundary layer (PBL) (e.g. Neuman et
58 al., 2016; Peng et al., 2020). Satellite detections have been reported for the IASI instrument in
59 Australian fires in 2009 and 2019 (Clarisse et al., 2011; Longueville et al., 2021) and an estimation
60 of HONO volume mixing ratio (vmr) in the 2009 plume is provided over sea by Armante et al.
61 (2021). Recently, TROPOMI has shown capabilities to cartography the HONO emitted by fires

62 (Theys et al., 2020). The aforementioned study is restricted to regions close to the sources and
63 does not show any tracking of HONO in dispersed fire plumes over sea. In the present study, we
64 focus on satellite-based detection of HONO during the record-breaking 2019/2020 Australian
65 bushfire season (also called the Australian Black Summer). These mega forest fires burnt an
66 unprecedented area of about 5.8 million hectares, which is more than 20% of whole Australian
67 temperate forests amount (Boer et al., 2020). This historically-relevant fire season was active from
68 September 2019 to March 2020. The concentrations of many tropospheric pollutants were
69 enhanced, in the Southern Hemisphere, since the early phases of the fire season (Kloss et al., 2021).
70 By the way, the intensity of the fires escalated and had a peak in intensity starting from New Year's
71 Eve 2019/2020 to early January 2020, and led to extreme pyro-convective clouds events and the
72 formation of a self-sustained smoke-charged vortex that polluted the stratospheric trace gases and
73 aerosol composition at the Hemispheric spatial scale (Khaykin et al., 2020). We report here on
74 HONO plume detections and transport at relatively high altitude (free troposphere) using
75 successive overpasses of 4 infrared (IR) sounders i.e. CrIS and a series of IASI instruments, during
76 the most intense phase of the 2019/2020 Australian fires in early January 2020. For the first time,
77 HONO has been quantified along the plume transport almost during 24 hours after emission. The
78 CHIMERE chemistry-transport model (CTM) is used to quantify the processes leading to such a
79 plume. In Section 2, we describe the satellite instruments, the detection and retrieval methods as
80 well as the model and simulations experiments performed. In Section 3, a description of the HONO
81 plume crossing the Tasman Sea at free tropospheric levels is given by the observations and the
82 model. The dominant chemical processes leading to such an event is discussed. Conclusions are
83 drawn afterwards.

84 **2 Data and Methods**

85 **2.1 IASI**

86 The IASI (Infrared Atmospheric Sounding Interferometer) instruments are nadir-viewing
87 Fourier transform spectrometers (Clerbaux et al., 2009). Three versions of the instrument are
88 currently flying on board the EUMETSAT (European Organisation for the Exploitation of
89 Meteorological Satellites) Metop satellites on a morning orbit (9:30LST and 21:30LST equator
90 crossing times): one aboard the Metop-A platform since October 2006, one aboard the Metop-B
91 platform since September 2012, and one aboard the Metop-C platform since November 2018. The
92 IASI instruments operate in the thermal infrared between 645 and 2760 cm^{-1} with an apodized
93 resolution of 0.5 cm^{-1} and a radiometric noise of about 0.2K around 1000 cm^{-1} . Each IASI
94 instrument scans the atmosphere with a swath width of 2200 km, allowing a global coverage twice
95 a day, with a field of view of 2×2 pixels with 12 km footprint at nadir. Metop-A, Metop-B, and
96 Metop-C temporal difference is ~ 30 min.

97 **2.2 CrIS**

98 The CrIS (Cross-track Infrared Sounder) instrument is a Fourier transform spectrometer
99 aboard the Suomi National Polar-orbiting Partnership (S-NPP) platform, in a sun-synchronous low
100 Earth orbit with overpass times of $\sim 01:30$ and $13:30$ local time. Two CrIS instruments are flying,
101 the first one since October 2011 and the second one since November 2017. In this study, we use
102 the first of these. CrIS scans the atmosphere with a swath width of 2200 km and a field of view of
103 3×3 pixels of 14 km diameter at nadir. CrIS is a hyperspectral infrared instrument with an

104 unapodized spectral resolution of 0.625 cm^{-1} and low spectral noise of $\sim 0.04\text{K}$ in its long-wave
105 infrared band 1 ($648.75\text{-}1096.25\text{ cm}^{-1}$) (Han et al., 2013; Strow et al., 2013; Tobin et al., 2013).

106 2.3 HONO spectral ratio and retrieval method

107 We use the spectral window between 785 and 795 cm^{-1} for HONO detection and retrievals
108 (Fig. S1). For HONO the spectroscopic parameters originate from a preliminary version of the
109 linelist for the ν_4 bands of the HONO Trans- and Cis- conformers that is now available in the
110 GEISA database (Armante et al., 2021; Delahaye et al., 2021). The selected $785\text{-}795\text{ cm}^{-1}$
111 microwindow corresponds to the HONO trans- ν_4 band, where the line intensities are about 12%
112 larger than in Armante et al. (2021). This is largely within the estimated accuracy associated to
113 this entity (about 30%). Carbon dioxide and water vapor are the two main interferers in this
114 window. Their spectroscopic data are taken from HITRAN 2004 (Rothman et al., 2005).

115 The HONO detection is based on the spectral ratio between one wavenumber belonging in
116 the HONO trans- ν_4 absorption band and one without HONO and interferers absorption. As IASI
117 and CrIS spectra have different spectral resolution and the IASI spectra are apodized while CrIS
118 spectra are not, we use different definition of the spectral ratio: it is the ratio between the radiances
119 at 790.5 and 789.0 cm^{-1} for IASI and at 790.0 and 788.75 cm^{-1} for CrIS. For this ratio, a threshold
120 is fixed at 0.985 as a first rapid detection of the scenes and days of interest. Then, to spatially
121 delimit the plumes, we use the distribution of the spectral ratios according to the radiance values
122 (Fig S2). Pixels are considered within the HONO plume when their spectral ratio is smaller than
123 the mean of the distribution minus 3σ for the corresponding radiance. The retrieval is performed
124 for the pixels characterized by a positive detection (i.e., the ones individuated as within the plume).
125 For these pixels, the radiative transfer (RT) is modeled using the KOPRA RT model (Stiller et al.,
126 2000) and the retrieval is performed by its inversion module, KOPRAFIT. The lack of information
127 on the HONO variability and vertical distribution in fire plumes does not permit to derive a
128 meaningful covariance matrix for the retrieval. We then use a smoothing constraint following
129 Steck (2002). We use the discrete first-derivative operator as the constraint operator and fix the
130 strength of the constraint to have one degree of freedom for the solution. A vertically constant a
131 priori profile is used. The CO_2 and H_2O absorption lines are simultaneously fitted with HONO.
132 The HONO (vertically constant) retrieved volume mixing ratio provides an estimation of the
133 HONO volume mixing ratio for each in-plume pixel, knowing that the maximum of sensitivity
134 ranges from 5 to 15 km altitude according to the averaging kernels. It is worth noting that, due to
135 the particular conditions in the plume (e.g. smoke contamination), convergence of the retrievals is
136 reached for a fraction of all the available pixels..

137 2.4 CHIMERE

138 CHIMERE v2020r1 is used over a large Australian domain with a horizontal resolution of 25×25
139 km^2 extending from -56 to 10°N and 105 to 178°E . The vertical resolution is 15 levels from the
140 ground to 300 hPa . It is driven by WRF regional model version 3.7.1 (Skamarock et al., 2008). A
141 full description of WRF-CHIMERE is available in Menut et al. (2021). CAMS global
142 anthropogenic v4.1 emissions (Granier et al., 2019) for the year 2019 are used. HONO
143 anthropogenic emissions are considered as 1.5% of NO_x emissions from traffic and 0.5% of NO_x
144 from other sectors. Fire emissions from CAMS GFAS (Kaiser et al., 2012) are considered. No
145 diurnal cycle is applied. The injection height is calculated by the Sofiev et al. (2012) scheme. 80%
146 of the mass is injected around this height and 20% from the ground to this height. NO_x fire

147 emissions are divided into 90% of NO and 10% of NO₂. The HONO gaseous chemistry is
 148 represented by MELCHIOR2 chemical mechanism described in Menut et al. (2013). HONO
 149 heterogeneous formation from NO₂ deposition on wet surface is considered, using the Aumont et
 150 al. (2003) formulation. The different reactions (R1-R5) are listed in Table 1. This constitutes the
 151 reference simulation of the study, named simulation GFAS (Table 1). However, the observed
 152 HONO/NO₂ ratio close to fire sources suggests that HONO primary emissions can be very high
 153 (Theys et al., 2020). In a second simulation, named HONOMAX, we added HONO wildfire
 154 emissions as 61% of NO_x emissions from GFAS. This corresponds to the upper range of
 155 HONO/NO₂ enhancement ratios observed by Theys et al. (2020). In addition, many studies have
 156 suggested an additional source of HONO would be present in the daytime as said before (e.g.
 157 Wong et al., 2013). To account for this formation pathway, we added a photolytic HONO
 158 formation on aerosol (R6) in a third simulation, named HONOMAXJ (Table 1). The effect of the
 159 photolysis is considered as zenithal angle function. For urban Chinese conditions, at local noon,
 160 Lu et al. (2018) derived for the collision (reactive uptake) coefficient a range of values from 1 to
 161 $8 \cdot 10^{-4}$. We retained here a collision coefficient of 10^{-3} (γ in Table 1), for local noon, which is
 162 slightly above the upper range of these estimations and also an order of magnitude larger than the
 163 value chosen in Liu et al. (2021) for model simulations in Beijing. All three simulations include
 164 the light independent heterogeneous HONO formation pathway. Finally, to quantify the
 165 importance of each process, we have added some reactive tracers. Each tracer has the same sinks
 166 (chemistry and deposition) as real HONO species. Only the source of each tracer is different:
 167 HONO_FIRE for primary fire emissions, HONO_ANT for CAMS anthropogenic emissions,
 168 HONO_CHEM for (R1), HONO_SURF for (R4), HONO_AER for (R5), and HONO_AERJ for
 169 (R6).

170 **Table 1.** List of reactions involving HONO included in the CHIMERE simulations and description
 171 of the CHIMERE simulations.

R1	NO+OH+M→HONO	$k = \frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}} f^p$ $p = \frac{1}{1 + \left(\log_{10} \left(\frac{k_0[M]}{k_\infty} \right) \right)^2}$ $k_0 = A_0 e^{\left(-\frac{B_0}{T} \right)} \left(\frac{T}{300} \right)^{-n_0}$ $k_\infty = A_\infty e^{\left(-\frac{B_\infty}{T} \right)} \left(\frac{T}{300} \right)^{-n_\infty}$ $A_0 = 7 \times 10^{-31}, B_0 = 0, n_0 = 2.6$ $A_\infty = 1.5 \times 10^{-11}, B_\infty = 0, n_\infty = 0.5$ $f = 0.6$	Atkinson et al. (1997)
R2	HONO+OH→NO ₂	$k(T) = A e^{-B/T}$ $A = 1.8 \times 10^{-11}, B = 390$	Atkinson et al. (1997)
R3	HONO+hν→NO+OH	J _{HONO}	Burkholder et al. (2010)
R4	NO ₂ →HONO	ks=0.5*depo(NO ₂)	Aumont et al., 2003

R5	$\text{NO}_2 \rightarrow 0.5 \cdot \text{HONO} + 0.5 \cdot \text{HNO}_3$	$k_{\text{NO}_2} = \frac{1}{4} \gamma \langle c \rangle S_a$ $\gamma = 5 \times 10^{-5}$	Tang et al., (2014)
R6	$\text{NO}_2 + h\nu \rightarrow \text{HONO}$	$k_{\text{NO}_2} = \frac{1}{4} \gamma \langle c \rangle S_a \max(\cos(\theta_s), 0)$ $\gamma = 1 \times 10^{-3}$	Wong et al., (2013)
Simulation GFAS		R1-R5 and GFAS emissions	
Simulation HONOMAX		Simulation GFAS + HONO primary emissions as 61% of NO _x	
Simulation HONOMAXJ		Simulation HONOMAX + R6	

172

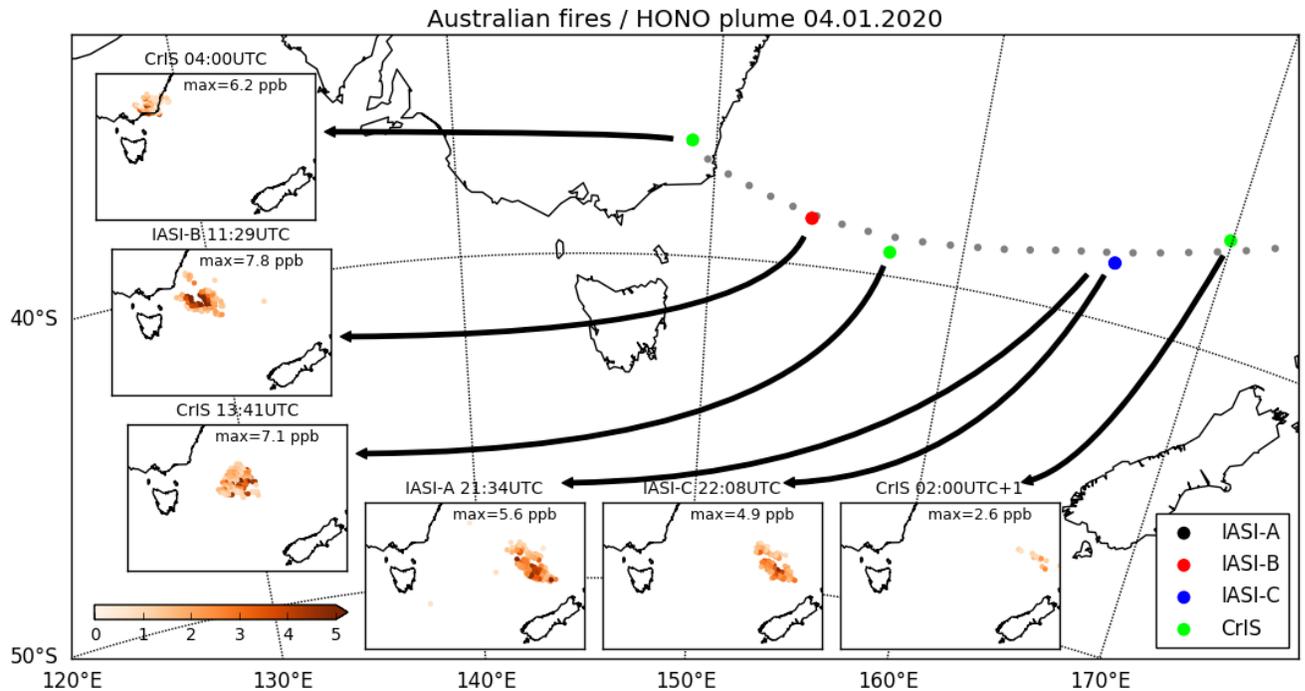
173 **3 Results and discussion**

174 3.1 HONO plume detection and tracking from satellite observations

175 The rapid preliminary screening detection procedure based on the spectral ratio has been
176 first applied to the entire IASI-A archive since 2007. Two main HONO detections have been found
177 during the 2009 Australian fires already reported in literature (Armante et al., 2021; Clarisse et al.,
178 2011) and during the record-breaking Australian fires, which occurred from the end of 2019 to
179 early 2020. For the latter where an intense and well-shaped plume has been detected on 4 January
180 2020 and is subsequently analyzed in detail. Using combined IASI-A, IASI-B, IASI-C, and CrIS
181 data, we are able for the first time to follow a HONO fire plume over a full day with several
182 overpasses, which enables us to follow the temporal evolution of its concentrations. We are then
183 able to track the plume from Southeast Australia (South of Canberra) on 4 January 2020 04:00
184 UTC to West of the northern edge of New-Zealand on 5 January 2020 02:00 UTC across the
185 Tasman Sea. We consider the detected plume only where it is fully sampled by the satellite
186 instruments (in the middle of the swath and not in the border). Figure 1 shows the plume trajectory
187 and displays the HONO vmr observed during the plume transport. The plume forward trajectory
188 is calculated with the HYSPLIT model (Rolph et al., 2017; Stein et al., 2015) initialized at the
189 mean location (latitude, longitude) of the plume detected by CrIS at 04:00 UTC and constrained
190 by the Global Data Assimilation System (GDAS). As the satellite observations are broadly
191 sensitive from 5 to 15 km, we tested different initialization heights and searched for the ones
192 matching the center of the plume detected with IASI and CrIS for the following 24 hours. Both 7
193 km and 9 km initializations succeed to reproduce the satellite-based trajectory. When initialized at
194 7 km the air mass remains within 6 and 7 km during the plume transport to New-Zealand a day
195 after. At 9 km, the air mass is rapidly uplifted between 11 and 12 km and then moved on at constant
196 altitude (Fig. S3). The height of the plume in the free or upper troposphere is consistent with the
197 detection capabilities of the IR sounders, which are mostly sensitive to this atmospheric region due
198 to large temperature differences with respect to the surface. It is also worth noting that in January
199 2020 extreme pyro-convection kicked-off, linked to this fire event, leading to the injection of fire-
200 related gaseous and particulate emissions in the stratosphere, at altitudes larger than 17 km
201 (Khaykin et al., 2020). The smoke-charged vortex plume was lifted, in the following two months,
202 by in-plume radiative heating to altitudes as high as 35 km. The initial uplifting tendency of the
203 plume is also visible in our present trajectories analyses. Unfortunately, CALIOP measurements
204 are not available for that day to help identifying the plume height.

205 Figure 1 shows the evolution of the HONO vmr during the transport of the plume from
206 Southeast Australia to New-Zealand. HONO vmr increases between 4UTC and 11UTC when night
207 starts. Then, a slow decrease is observed from sunrise onwards when HONO is photolyzed but
208 with observed vmr still higher than 1 ppb. As the retrievals may fail when aerosol load is strong,
209 typically at the center of the plume, and lead to an underestimation of mean HONO concentrations
210 we also consider in the following the 90-percentile, which is more representative of the central
211 region of the plume where dilution with background air is reduced and the aerosol light extinction
212 is larger reducing HONO photolysis (during daytime) (Peng et al., 2020). The retrieved
213 concentrations range between 1.3 to 2.9 ppb on average, 2.1 to 5.5 ppb in the center of the plume
214 (90-percentile) (Fig. 3, red symbols). It is worth noting these vmrs are consistent with the HONO
215 vmrs estimated in the 2009 plume by Armante et al. (2021). In 2020, the concentrations increase
216 during the night and reach 2.9 ppb on average, 5.5 ppb in the center of the plume at 11:30UTC and
217 then start to decrease progressively when sun rises and drop to 1.3 ppb on average (2.1 in the center
218 of the plume) at 2UTC on 5 January 2020. This range of concentrations are consistent with HONO
219 concentrations measured in fire plumes, mainly in the U.S, during field and airborne campaigns
220 (e.g. Neuman et al., 2016; Zarzana et al., 2017, Kaspari et al., 2021). However, compared to HONO
221 concentrations reported in the literature, the HONO concentrations retrieved from CrIS and IASI
222 likely correspond to plumes much higher in altitude than the ones sampled during airborne
223 campaigns, so that they are not clearly comparable. The fuel power of the 2019/2020 Australian
224 fire was likely strong enough to emit large quantities of NO_x and HONO and to uplift the emitted
225 fire products higher than usual in the atmosphere, allowing a better detection from IR sounders.
226 Satellite observations show production of HONO within the plume during the night, as HONO
227 concentrations increase albeit plume diffusion. Then, significant HONO concentrations (about the
228 half of the maximal nighttime values) surprisingly remain in the plume even after sunrise,
229 suggesting that HONO photolysis may be counterbalanced by production within the plume. Such
230 a mechanism has been recently reported by Kaspari et al. (2021) but for measurements near the
231 surface where the heterogeneous secondary production of HONO is increased by the ground
232 surface.

233



234

235 Figure 1. HONO plume tracking by CrIS and IASI instrument. HYSPLIT trajectory

236 (initialized at 7 km – similar when initialized at 9 km). Normalized spectral ratios.

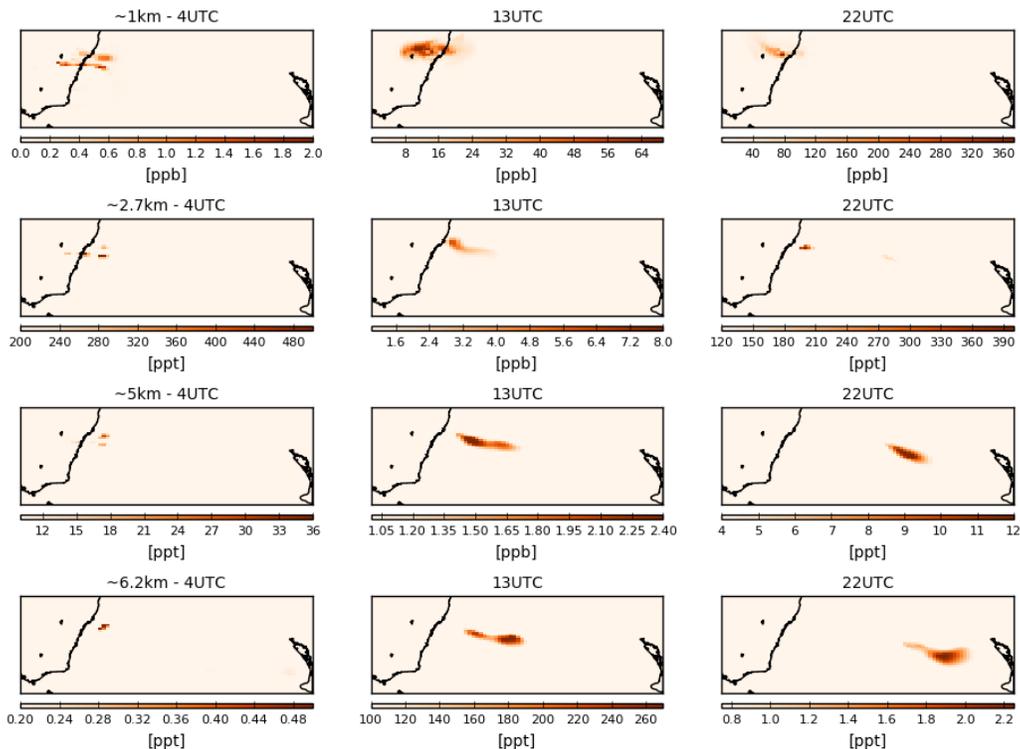
237

3.2 Simulated HONO plume with CHIMERE

238

We use the CTM CHIMERE to simulate HONO in the 2019/2020 Australian fires as described in section 2.4. Simulating correct HONO concentrations is a great challenge for models due to the large uncertainties in the fire emissions (location, intensity, emission factors, injection height etc), their HONO fraction, and plume chemistry, in particular heterogeneous HONO formation, photo-induced or not. CHIMERE simulations are then mainly used to evaluate different HONO temporal evolutions within the fire plume rather than absolute concentrations. For 4 January 2021, the model simulates a HONO plume similar to the one detected by the satellite instruments. The simulated plume starts in the vicinity of Canberra, northward compared to the observed plume (Fig. 2). The plume extends up to the level 12 of the model between 6 and 7 km. The upper part of the plume (level 11 around 5 km and level 12 between 6-7km) moves faster and further away above the Tasman Sea towards the western part of New Zealand. Due to the vertical sensitivity of IR sounders and the forward trajectories coherent with the detected plumes, we focus on these two levels for the analysis of the three simulations detailed in Section 2.4.

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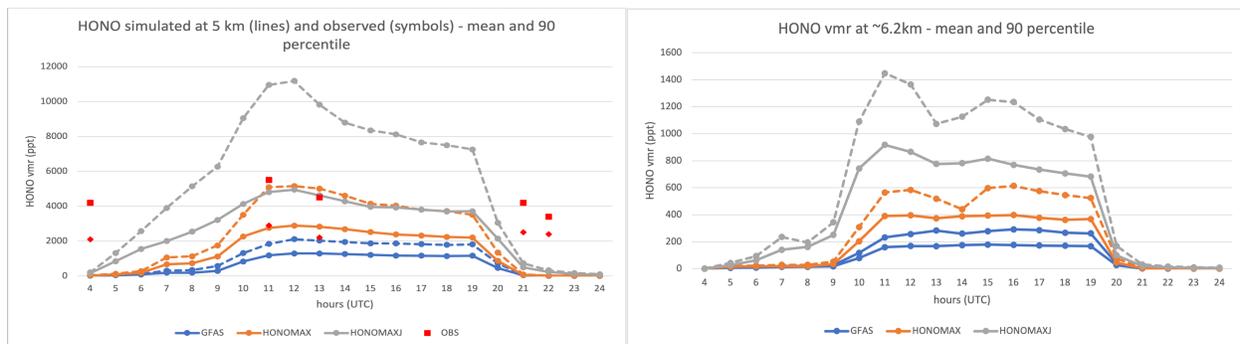


251
 252 Figure 2. Simulated HONO concentrations within the plume (simulation GFAS) at different levels
 253 (levels 5 (~1km), 9 (~2.7km), 11 (~5km), and 12 (~6.2km)) and hours of 4 January 2020.

254
 255 At the maximum, the HONO vmr simulated by the GFAS simulation reaches about 0.2 ppb in the
 256 plume at level 12 and 1.3 ppb on average (2 ppb for 90-percentile) at level 11 (Fig. 3). Compared
 257 to satellite observation, these concentrations are largely underestimated at level 12 (~6.2km),
 258 which is closer to the altitude range of the satellite sensitivity. When including the primary HONO
 259 emissions (HONOMAX), the HONO vmr increases to about 0.4 ppb on average in the plume (0.6
 260 ppb 90-percentile) at level 12 and to about 3 ppb on average (5 ppb 90-percentile) at level 11.
 261 Including the heterogeneous photo-induced reaction of NO_2 increases HONO levels closer to 1
 262 ppb (1.4 ppb 90-percentile) at level 12 and then closer to the order of magnitude of HONO
 263 observed by IR sounders. At level 11, HONO reaches at maximum 5 ppb (11 ppb 90-percentile)
 264 when this reaction is considered. However, because of the uncertainty in injection height, it is not
 265 possible to favor one of the three simulations from this first comparison. In terms of process
 266 contributions, the photo-induced heterogeneous reaction dominates the HONO production in the
 267 plume when included, followed by HONO_AER (light independent heterogeneous reaction) and
 268 the contribution from primary emissions (Fig. S4). Analyzing the temporal evolution shows
 269 interesting differences between the three simulations (Fig. 3). They all show a rapid increase of
 270 HONO at the night between 9 and 11 UTC. The increase is more progressive at level 11 especially
 271 for the HONOMAXJ simulation because HONO is formed more strongly at the end of the first

272 day due to the photo-induced heterogeneous reaction. An abrupt decrease is observed for all the
 273 simulations between 19 and 20 UTC, at the beginning of the next day. While HONO
 274 concentrations without a photo-induced HONO source rapidly drop to near zero at day time, the
 275 one including such a source shows significant HONO levels for the early morning hours, about 0.5
 276 (average) to 0.8 ppb (P90) at level 11 at 21 UTC. However later on, they also show HONO
 277 concentrations close to zero (few ppt or less). The amplitude of this drop-off is much stronger than
 278 the one observed with the data, even for the simulation including the photo-induced reaction. This
 279 could either suggest a model overestimation of HONO sinks (i), or of HONO plume dilution (ii),
 280 or an underestimation of HONO sources. Concerning HONO photodissociation the aerosol
 281 induced actinic flux attenuation is included in the model, but the photodissociation rate may be
 282 biased high, if aerosol mass is biased low. Dilution of the plume certainly plays a role in reducing
 283 HONO levels, but this process is expected to happen continuously and not only at sunrise. Finally,
 284 our study suggests the possibility the photoinduced collision coefficient (R6) of 10^{-3} (at cloud free
 285 local noon), at the upper end of values given in available literature (10^{-4} - 10^{-3} as discussed in section
 286 2.4), might still be underestimated. Alternatively or in addition, available aerosol surface might be
 287 higher than estimated by our model assuming spherical particles. For example, fire aerosol can be
 288 highly porous through the formation of soot aggregates (Chakrabarty et al., 2014). These
 289 hypotheses warrant for further studies.

290



291

292 Figure 3. Temporal evolution of HONO simulated at 11km and 12km by CHIMERE for the three
 293 simulation experiments described in Table 1. Mean vmr are represented as full lines and 90-
 294 percentile vmr as dashed lines.

295 Conclusions

296 For the first time, a HONO plume emitted by the record-breaking 2019/2020 Australian
 297 fires has been tracked, and its evolution quantified, during one day above the Tasman Sea by four
 298 IR sounders, the three IASI and CrIS. HONO vmrs of several ppb have been retrieved within the
 299 plume. The remarkable points rise from the transport at free tropospheric altitudes (or higher) of
 300 the plumes (or higher) and the persistence of large HONO vmr (>1ppb) after one day during
 301 sunrise. Model simulations, aiming at reproducing this exceptional event, confirm that the plume
 302 is transported in the free troposphere and suggest a significant contribution of primary fire
 303 emissions of HONO and of photo-induced heterogeneous reactions to explain the observed HONO
 304 vmrs. However, despite this, the question of the processes involved to explain the persistent HONO
 305 concentrations at sunrise is not fully resolved, the model showing a much stronger decrease of

306 HONO when the sun rises, which points to remaining unknowns in chemistry and aerosol loading
307 in the plume.

308

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320

321 **Open Research**

322 The IASI Level 1C data used for the HONO observations in fire plumes in the study are
323 available at the French Data and Service for the Atmosphere (AERIS) portal via [https://iasi.aeris-](https://iasi.aeris-data.fr/)
324 [data.fr/](https://iasi.aeris-data.fr/) with registration.

325 The CrIS Level 1 data used for the HONO observations in fire plumes in the study are available
326 at the GES DISC NASA portal via

327 https://sounder.gesdisc.eosdis.nasa.gov/data/SNPP_Sounder_Level1/SNPPCrISL1BNSR.2/ with
328 registration.

329 V2020r1 of the CHIMERE model used for simulating HONO in Australian fire plumes is
330 preserved at <https://www.lmd.polytechnique.fr/chimere/>, available via the GNU General Public
331 License with registration and developed openly at <https://www.lmd.polytechnique.fr/chimere/>.

332 The emission inventory data used for the HONO simulations as input of the CHIMERE model
333 are available at the French Data and Service for the Atmosphere (AERIS) portal via
334 <https://eccad.aeris-data.fr/> with registration.

335 Version 5.1.0 of the HYSPLIT transport and dispersion model used to calculate trajectories of
336 fire plumes in this study is preserved at <https://www.ready.noaa.gov>, available openly through
337 the website and developed openly at <https://www.ready.noaa.gov>.

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