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Annual Appearance of Hydrogen Chloride on Mars and a Striking Similarity With the Water Vapor Vertical Distribution Observed by TGO/NOMAD

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2 **Annual appearance of hydrogen chloride on Mars and a striking similarity with the**
3 **water vapor vertical distribution observed by TGO/NOMAD**

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37 **Key Points (< 140 char. for each):**

- 38 • Increase of HCl during the southern summer is annually repeated. It shows that HCl
39 formation is independent from a global dust storm.
- 40 • Vertical distributions of HCl are strikingly similar to water vapor. It suggests that uptake
41 by water ice clouds plays an important role.
- 42 • A rapid decrease of HCl at the end of the southern summer suggests the presence of a
43 strong sink in addition to the photochemical loss.
44

45 **Abstract**

46 Hydrogen chloride (HCl) was recently discovered in the atmosphere of Mars by two
47 spectrometers onboard the ExoMars Trace Gas Orbiter. The reported detection made in Martian
48 Year 34 was transient, present several months after the global dust storm during the southern
49 summer season. Here we present the full dataset of vertically resolved HCl detections obtained
50 by the NOMAD instrument, which covers also Martian year 35. We show that the particular
51 increase of HCl abundances in the southern summer season is annually repeated, and that the
52 formation of HCl is independent from a global dust storm event. We also find that the vertical
53 distribution of HCl is strikingly similar to that of water vapor, which suggests that the uptake by
54 water ice clouds plays an important role. The observed rapid decrease of HCl abundances at the
55 end of the southern summer would require a strong sink independent of photochemical loss.

56

57

58 **Plain Language Summary**

59 A new species, hydrogen chloride (HCl), was recently discovered in the atmosphere Mars.
60 Whereas this gas plays a key role in the atmospheric chemistry on Earth and Venus, the chlorine
61 cycle on Mars is not understood. HCl was found just after the global dust storm, so a connection
62 between the storm and appearance of HCl was suggested. This study shows that HCl is detected
63 even in a year without a global dust storm, which demonstrates that the formation of HCl is
64 primary independent from global dust storms. This study also finds that the vertical distributions
65 of HCl and water vapor are strikingly similar in shape. As the vertical profile of water vapor is
66 controlled by the formation of water ice clouds, it suggests that HCl is taken up by water ice
67 clouds. Finally, we observe that HCl is rapidly disappearing at the end of the southern summer
68 on Mars. We demonstrate that this fast destruction cannot be explained by the standard
69 photochemistry, which suggests that another (unknown) process plays a key role.

70

71 **1. Introduction**

72 Chlorine chemistry plays an important role in the atmosphere of Earth and Venus. On
73 Earth, small amounts of chlorine can have a dramatic impact on stratospheric ozone (e.g.
74 Solomon, 1999). On Venus, chlorine is involved in the main photochemical cycles (e.g. Mahieux
75 et al., 2015; Sandor and Clancy, 2018). In contrast, on Mars, chlorine photochemistry was
76 considered to be negligible because of the low upper limits provided by the previous
77 measurements (Krasnopolsky et al., 1997; Hartogh et al., 2010; Villanueva et al., 2013).
78 However, the first detection of hydrogen chloride (HCl) in the atmosphere of Mars was made by
79 the Atmospheric Chemistry Suite (ACS) and also confirmed by the Nadir and Occultation for
80 Mars Discovery (NOMAD) onboard the ESA-Roskosmos ExoMars Trace Gas Orbiter (TGO)
81 (Korablev et al., 2021). This discovery of HCl is the first detection of any chlorine species in the
82 Martian atmosphere. It demonstrates an active presence of chlorine photochemistry and HCl is
83 expected to be the main reservoir of chlorine species in the atmosphere of Mars (Lefèvre and
84 Krasnopolsky, 2017). Perchlorate salts ClO_4^- (Hecht et al., 2009; Glavin et al., 2013) and
85 chloride-bearing minerals Cl^- (Osterloo et al., 2008, 2010) are known to be widely present at the

86 Mars surface, thus an interaction between surface and atmosphere may support chlorine
87 photochemistry. Model and laboratory studies investigated the potential role of atmospheric
88 photochemical processes in the formation of perchlorates (e.g. Catling et al., 2010; Smith et al.,
89 2014; Wilson et al., 2016; Wu et al., 2018, and references therein). However, the chlorine cycle
90 on Mars is still not understood. The discovery made by Korablev et al. (2021) hints at the
91 transient nature of HCl: the detections are mainly confined after the global dust storm in the
92 southern summer season. The observed fast temporal variation can be a key to identify the
93 formation and destruction mechanisms of HCl. The discovery was based on the data taken in
94 Martian year (MY) 34. This study presents the results of the extended NOMAD dataset that also
95 includes almost the full MY 35. We investigate the vertical distribution of HCl volume mixing
96 ratios (vmr) and their similarities with simultaneously obtained water vapor and aerosol profiles.
97 An analysis of the Cl isotopic ratio in HCl with the NOMAD data is presented in an
98 accompanying paper (Luizzi et al., 2021).

99 **2. Methods**

100 **2.1 Instrument - NOMAD onboard TGO**

101 NOMAD, a spectrometer operating in the spectral ranges between 0.2 and 4.3 μm
102 onboard ExoMars TGO (Vandaele et al., 2018), has 3 spectral channels: a solar occultation
103 channel (SO – Solar Occultation; 2.3–4.3 μm), a second infrared channel capable of nadir, solar
104 occultation, and limb sounding (LNO – Limb Nadir and solar Occultation; 2.3–3.8 μm), and an
105 ultraviolet/visible channel (UVIS – Ultraviolet and Visible Spectrometer, 200–650 nm). The
106 infrared channels (SO and LNO) have relatively high spectral resolution ($\lambda/d\lambda \sim 10,000\text{--}20,000$)
107 provided by an echelle grating used in combination with an Acousto Optical Tunable Filter
108 (AOTF) which selects diffraction orders (Neefs et al., 2015). The sampling rate for the solar
109 occultation measurement is 1 second, which provides high vertical sampling (~ 1 km) with high
110 vertical resolution (~ 2 km) from near the surface to 200 km altitude. Thanks to the instantaneous
111 change of the observing diffraction orders achieved by the AOTF, the SO channel is able to
112 measure five or six different diffraction orders per second in solar occultation mode. One of the
113 most remarkable capabilities of NOMAD is its high spectral resolution in the infrared range. This
114 supports investigations of: (1) vertical profiles for atmospheric constituents such as carbon
115 dioxide, carbon monoxide, water vapor, and their isotopic ratios (Vandaele et al., 2019; Aoki et
116 al., 2019; Villanueva et al., 2020); and (2) sensitive searches for organic species (such as CH_4 ,
117 C_2H_4 , C_2H_6 , H_2CO ; Korablev et al., 2019; Knutsen et al. 2021) and other trace gases (such as
118 HCl, HCN, HO_2 , H_2S , N_2O , OCS) by solar occultation measurements with the SO channel. In
119 this study, we analyze the solar occultation measurements acquired by the NOMAD SO channel
120 during the period from 22 April 2018 to 18 December 2020 (from a solar longitude (L_s) of 163°
121 in MY 34 to $L_s = 333^\circ$ in MY 35), which covers southern summer periods in MY 34 and 35. For
122 the current study, a total of 732 occultations that include diffraction order 129 ($2889\text{--}2921\text{ cm}^{-1}$)
123 or 130 ($2920\text{--}2943\text{ cm}^{-1}$) have been processed. These two diffraction orders contain a strong HCl
124 line (see **Figure 1**) and are normally acquired together with diffraction order 134 ($3010\text{--}3034\text{ cm}^{-1}$)
125 1), order 136 ($3056\text{--}3080\text{ cm}^{-1}$), or order 145 ($3258\text{--}3284\text{ cm}^{-1}$), which include strong water lines
126 in support of direct comparisons between HCl and water vapor vertical profiles.

127

128

2.2 Retrieval of HCl and water vapor volume mixing ratio

129 The reduction and analysis of the NOMAD data is basically conducted with the same
 130 methodology as the previous water vapor study (Vandaele et al., 2019; Aoki et al., 2019). The
 131 retrievals of HCl and H₂O are performed with the ASIMUT-ALVL radiative transfer and
 132 inversion code (Vandaele et al., 2006). H₂O, HDO, CO₂ and HCl molecular absorptions are taken
 133 into account in the radiative transfer calculation and the absorptions are calculated using the
 134 following spectroscopic database: HITRAN 2016 database (Gordon et al. 2016) for CO₂ and
 135 HCl, and the water line list for CO₂-rich atmospheres by Gamache et al. (2016) for H₂O and
 136 HDO. The temperature, pressure, and CO₂ volume mixing ratio of the simulated atmosphere is
 137 obtained from the Global Environmental Multiscale Mars model (GEM-Mars) (Neary and
 138 Daerden, 2018; Daerden et al., 2019) which takes into account the effects of the global dust
 139 storm in MY34 (Neary et al., 2020). The HCl and H₂O retrievals are performed using the
 140 Optimal Estimation Method (OEM) (Rodgers, 2000) for each spectrum at each tangential
 141 altitude independently. The retrieved HCl and H₂O abundances are finally averaged with an
 142 interval of 2 km to obtain the vertical profiles. The averages are weighted by their standard errors
 143 (weighted average). In addition to the HCl and H₂O abundances, the vertical profiles of aerosols
 144 extinction are investigated. The extinction profiles are simply derived from the averaged
 145 transmittances (at diffraction order 129 or 130) based on the onion-peeling method (Wilquet et
 146 al., 2012). **Figure 1** shows an example of the NOMAD spectra at diffraction order 129 (**Fig. 1a**)
 147 and order 130 (**Fig. 1b**). Clear signatures of HCl are identified at 2906.24 cm⁻¹ in order 129 and
 148 2925.89 cm⁻¹ in order 130. HCl is usually detected in the lower atmosphere (< 20-25 km) but
 149 sometimes up to 35-40 km altitude as shown in **Fig 1b**.

150 3. Results

151 3.1 Seasonal, spatial, and interannual variations of HCl

152 **Figures 2a-c** show the season-latitude maps of the maximum HCl volume mixing ratio
 153 below 30 km observed by NOMAD in MY 34 (**Fig. 2a**), MY 35 (**Fig. 2b**), and plotted together
 154 (**Fig. 2c**). As shown in Korablev et al. (2021), a few ppbv of transient HCl was detected in the
 155 Mars atmosphere. In MY 34, two strong dust storms occurred on Mars – the global dust storm at
 156 L_s=190°-250° and the regional dust storm at L_s=320°-340° (e.g., Aoki et al., 2019; Liuzzi et al.,
 157 2020). Almost all of the HCl detections were made in the period between the two dust storms
 158 (L_s=240°-320°) (**Fig. 2a**). The period of HCl detections also correspond to the southern summer
 159 season on Mars. The temporal variation of the HCl detections in MY 35 is similar to that in MY
 160 34: most of the HCl detections are made in the southern summer period (L_s=240°-320°) (**Fig.**
 161 **2b**). We use the dust climatology of MY 31 as a proxy, as it looks similar to that of MY 35. Since
 162 there is no global dust storm in MY35, it is demonstrated that the formation of HCl is
 163 independent from a global dust storm event. In both MY 34 and 35, higher abundances of HCl
 164 are observed in the southern hemisphere (local summer, L_s=270°), particularly at high latitudes,
 165 which corresponds in time and location to the water vapor enhancement caused by the south
 166 polar cap sublimation (**Fig. 2c**). Because the observations before L_s~240° were not possible in
 167 the southern hemisphere due to dust obscuration, it is unclear whether this represents an increase
 168 in HCl, or if high abundances were already present. In contrast, the volume mixing ratio of HCl
 169 is below the detection limit (~0.3 ppbv) at the northern hemisphere summer solstice (L_s=90°),
 170 even at high latitudes where the column integrated abundances of water vapor are large.

171 **Figure 2d** shows the geographical distribution of the maximum HCl volume mixing ratio
 172 below 30 km observed by NOMAD in the southern summer period (L_s=240°-320°) of MY 34

173 and 35. The detections are dispersed over all observed longitudes, such that HCl is not confined
174 to a specific longitude region. Most of the detections are performed at latitudes higher than 45° .
175 This is because higher dust content in the atmosphere at lower latitudes obscures solar
176 occultation viewing. In other words, the non-detection of HCl at low-latitudes means that the
177 abundance of HCl cannot be measured there. There is a clear north-south asymmetry – the
178 maximum volume mixing ratio of HCl is larger in the southern hemisphere than in the northern
179 hemisphere.

180

181

3.2 Vertical distribution of hydrogen chloride, water vapor, and aerosols

182 **Figure 3** shows several representative vertical profiles of HCl, water vapor, and aerosol
183 extinction observed during the same occultation. The seasonal variations of the HCl vertical
184 distributions measured in MY 34 and 35 are quite similar. At northern mid-latitudes (50° - 60° N)
185 around perihelion ($L_s=240^\circ$ - 270°) (**Fig. 3a**), water vapor volume mixing ratios increased towards
186 the higher altitudes with a maximum around 30 km. This decrease below 30 km reflects water
187 vapor loss at lower altitudes due to the condensation over the seasonal polar cap (e.g. Daerden et
188 al., 2019). In MY 34, because of increased upper level transport associated with the global dust
189 storm, water is also enhanced at higher altitudes (Aoki et al., 2019; Neary et al., 2020; Fedorova
190 et al., 2020). HCl also shows a decrease towards lower altitudes. At the southern mid-to-high
191 latitudes (50° - 70° S) during the same period (**Fig. 3b**), water vapor volume mixing ratios are
192 constant throughout the atmosphere and HCl follows this same uniform distribution.

193 This constant mixing continues after perihelion ($L_s=270^\circ$ - 300°), although in MY 35,
194 water and HCl vmr start to decrease between 20-30 km (**Fig. 3c**). Note that in this seasonal range
195 at $L_s=270^\circ$ - 300° , we observe larger water vapor mixing ratios (because of the sublimation of the
196 south polar cap) as well as the largest observed HCl vmr (4 ppbv) both in MY 34 and 35.
197 Moreover, HCl is detected at the highest altitudes (35-40 km). Water vapor is still abundant in
198 the later period ($L_s=300^\circ$ - 330°) but rapidly drops above the hygropause, which is located around
199 15-20 km (**Fig. 3d**). Interestingly, HCl also dramatically drops at the same altitudes. Finally, in
200 the northern hemisphere during the summer solstice ($L_s=90^\circ$ - 120°) (**Fig. 3e**), HCl is not detected
201 anymore while a large amount of water vapor is observed at lower altitudes (below 10 km)
202 because of the sublimation of the northern polar cap. This is a low-dust season, and the upper
203 limit of HCl below 10 km is ~ 0.3 ppbv, which is well below the abundances detected in the
204 southern summer season.

205 Such a temporal variation of the HCl vertical profiles observed by NOMAD is consistent
206 with the simultaneous measurements by ACS reported earlier (Korablev et al., 2021). In this
207 study, we emphasize that the vertical structures of HCl and water vapor are strikingly similar.
208 **Fig. 4a-b** shows the HCl vmr against scaled water vapor vmr for all the HCl detections below 25
209 km. The water vapor mixing ratios in this figure were scaled for each profile by the ratio of the
210 partial column densities of HCl and water vapor below 25 km (see Supporting Information, SI,
211 Section S1, for more details). This scaling process comes down to shifting the upper and lower x-
212 axes in **Fig. 3** such that the lower part of the HCl and H_2O profiles are overlapping, and so
213 allows us to evaluate the similarity in the shapes of the vertical distributions. The partial column
214 densities were calculated using collocated GEM-Mars temperature and pressure profiles
215 (Daerden et al., 2019; Neary et al., 2020) for the altitudes where HCl was detected. It was
216 preferred to work with partial column densities rather than the ratio of the vmr at one specific

217 altitude level, because there is no unique altitude level at which HCl was detected in all the
218 profiles.

219 **Fig. 4a-b** demonstrates a strong similarity of the shapes of HCl and water vapor vertical
220 structures in the perihelion season. The water vapor profile is shaped by the formation of clouds
221 and their subsequent sedimentation over the course of one or many consecutive sols,
222 counteracting the ascend of water vapor with the normal circulation (Neary et al., 2020). This
223 causes a decrease of the water vapor vmr at the “hygropause” level (e.g., Daerden et al., 2019,
224 their Fig. 13). In polar winter conditions, the water vapor profile is also decreasing towards the
225 surface due to strong surface deposition. We see both types of profiles in Fig. 3. The similarity of
226 the HCl profiles to those of water vapor suggests that HCl is depositing with water vapor, both at
227 the hygropause and at the surface in polar winter. Laboratory work for temperatures (194-228 K)
228 and pressures (133 Pa) representative of Mars (Kippenberger et al., 2019), and for similar HCl
229 partial pressures as found here, demonstrated an extensive, continuous uptake of HCl in water ice
230 during growth of ice particles. This seems to indicate that HCl, once introduced in the
231 atmosphere, tracks with water vapor. However, this behavior does not address the ultimate
232 source or loss processes for Mars atmospheric HCl, as will be discussed below. When the ratio
233 HCl/H₂O is plotted for all the profiles combined, it is not decreasing over time and altitude (**Fig.**
234 **4c-d**). This could imply that the uptake of HCl on water ice clouds is not a permanent sink and
235 that HCl is released again when water ice sublimates. However, it can also mean that new
236 chlorine-bearing species are formed at the water ice cloud particles, that can become a new
237 source of HCl (see Discussion for more details).

238

239 **4. Discussion**

240 **4.1 Source of HCl**

241 The first detections of HCl were obtained mainly just after the MY 34 global dust storm.
242 Therefore, Korablev et al. (2021) proposed that dust – including chloride-bearing materials –
243 lifted to high altitudes could release chlorine into the atmosphere by UV irradiation. This would
244 ultimately lead to the formation of HCl through the fast reaction of chlorine with hydroperoxyl
245 that results from photolysis of water vapor also lifted to high altitudes (Wilson et al., 2016;
246 Lefèvre and Krasnopolsky, 2017):



247 However, the repeated detections of equivalent HCl abundances in the same season in
248 MY 35 clearly indicates that a global dust storm is not required, the annually enhanced dust
249 abundances in the perihelion season appearing to be sufficient to produce HCl.

250 The strong enhancement of HCl at the southern high latitudes in the southern summer
251 season suggests that the main source of atmospheric chlorine could be there. We note that further
252 measurement are needed to confirm the source as a large part of the NOMAD observations at
253 low- and mid-latitudes could not detect HCl because of strong dust presence. Nevertheless, if the
254 source is the southern high latitudes, the produced HCl can be transported to the northern
255 hemisphere by the global circulation. Theoretical studies show that the time scale of the global
256 mixing from 60°S latitude to north polar latitudes can be as low as 20 sols or less in this season

257 (Vaugh et al., 2019, their Fig. 1d). This is fast enough to explain the observed latitudinal
258 distribution of HCl.

259 The combination of enhanced dust and water abundances seems to be the key ingredient
260 for the production of HCl. This may explain why there is no HCl detected in the northern
261 summer season, which, despite the presence of large amounts of water vapor, is relatively dust-
262 free. HCl may still be there, but below the detection limit. Dust optical maps from Montabone et
263 al. (2015, 2020) show a ratio of dust optical depths between perihelion and aphelion of ~ 5 (even
264 in a low dust year), which could be sufficient to either preclude the formation of HCl in northern
265 summer, or to keep it below detectability. However, detection limits reported in Korablev et al.
266 (2021) (0.1-0.2 ppbv) and here (0.3 ppbv) are much lower than simply scaling the observed HCl
267 abundances by a factor of 5. It is possible that a certain threshold of dust abundance is required
268 for the formation of HCl. Another possibility is that the HCl is released from the southern polar
269 cap together with water vapor. But then the question remains why the same process is not
270 occurring at the northern summer cap. If chlorine species are stored in the seasonal caps and
271 released with water vapor during local spring and summer to form HCl, HCl should be strongly
272 present during northern summer, which is not the case.

273

274

4.2 Sink of HCl

275 Another important issue arising from the reported observations regards the relatively
276 rapid decay of atmospheric HCl abundances, requiring a strong HCl loss rate (Korablev et al.,
277 2021 and Fig. 2 of this article). Indeed, the photochemical lifetime of HCl in the low atmosphere
278 of Mars is estimated to be relatively long (see SI, Section S2). It can vary between >90 sols to
279 >1000 sols below 15 km at the southern and northern mid-latitudes during the northern
280 hemisphere winter solstice (see Fig. S2). On the other hand, the production of HCl through the
281 reaction between Cl and HO₂ is much faster (typically on timescales <10 minutes in the lower
282 atmosphere; see Fig. S2). As a result, HCl is expected to be the primary Cl reservoir species in
283 the Martian atmosphere. In this context, the sudden loss of HCl which is observed around
284 $L_s=320^\circ$ (**Fig. 2**) cannot be explained by gas-phase photochemistry alone. A sink process, in
285 addition to photochemical loss, has to be invoked. Korablev et al. (2021) suggested that HCl
286 could be removed from the atmosphere by uptake in growing water ice clouds particles and/or
287 surface ice (Kippenberger et al., 2019). The striking similarity between HCl and water vapor
288 vertical profiles shown in this study suggests that the vertical distribution of HCl is controlled by
289 water ice clouds. However, the sublimation of those ice particles would be accompanied by the
290 release of chlorine and thus the formation of atmospheric HCl, and thus it looks problematic to
291 explain the permanent removal of HCl from the atmosphere by the uptake of HCl (reversible or
292 irreversible) by water ice clouds.

293 Another possibility to remove HCl may be heterogeneous reactions on water ice cloud
294 particles. This process is well known on Earth, where such reactions play a role in the formation
295 of the polar ozone hole: $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$, $\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{ClNO}_2 + \text{HNO}_3$, HOCl
296 $+ \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ (Solomon, 1999). However, even if those reactions could take place
297 efficiently on Mars, the produced chlorinated compounds would be readily converted to Cl
298 radicals by photolysis (on timescales of a few tens of minutes), and subsequently create HCl by
299 Reaction (1). Chlorine can also be removed by the formation of perchlorates (ClO_4^-). The uptake
300 of ClO on ice particles was experimentally observed to lead to the release of chlorine dioxide
301 (OCIO) upon ice evaporation (McKeachie et al., 2004). Although the enhanced concentrations of

302 OClO could favor the production of HClO_4 (Catling et al., 2010; Wilson et al., 2016) and the
303 permanent removal of chlorine from the gas phase, this process should be much too slow to
304 explain the rapid loss of HCl.

305 It remains difficult to explain the disappearance of HCl after $L_s=320^\circ$. Interestingly, the
306 time of this sudden HCl loss corresponds to the onset of the regional storm (**Fig. 2**) that is
307 annually repeated and recognized as "c" dust storm. This raises the possibility that this dust
308 storm acts as the sink for HCl. In this respect, note that mineral dust was found to be the seat of
309 HCl removal in the Earth's atmosphere (Sullivan et al., 2007). However, these arguments require
310 robust dust-HCl interactions that are not yet established by laboratory studies, and so need to be
311 addressed in the future.

312 **5. Conclusions**

313 In this paper, we present the full dataset of vertically resolved HCl detections derived
314 from the TGO/NOMAD measurements taken between April 2018 and December 2020, which
315 covers southern summer periods in MY 34 and MY 35. The main results are as follows:

- 316 1. We find enhancement of HCl at the southern summer period ($L_s=240-320^\circ$) both in
317 MY 34 and MY 35. It suggests that the global dust storm (which occurred only in
318 MY 34) is not necessary for the formation of HCl.
- 319 2. Both in MY 34 and MY 35, a larger abundance of HCl is observed at the southern
320 high latitudes where water vapor sublimates from the southern polar cap.
- 321 3. We find that the vertical distributions of HCl and water vapor are strikingly similar in
322 shape. It suggests that once HCl is introduced in the atmosphere, it follows water
323 vapor including uptake in water ice clouds.
- 324 4. We show that the lifetime of HCl in the Mars atmosphere is too long to explain the
325 observed rapid loss of HCl in the Mars atmosphere around $L_s=320^\circ$, which thus
326 requires a strong sink of HCl independent from the photochemical loss.

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349 The NOMAD data used in this study are available from ESA’s Planetary Science Archive
350 at <https://archives.esac.esa.int/psa/#!Table%20View/NOMAD=instrument>.

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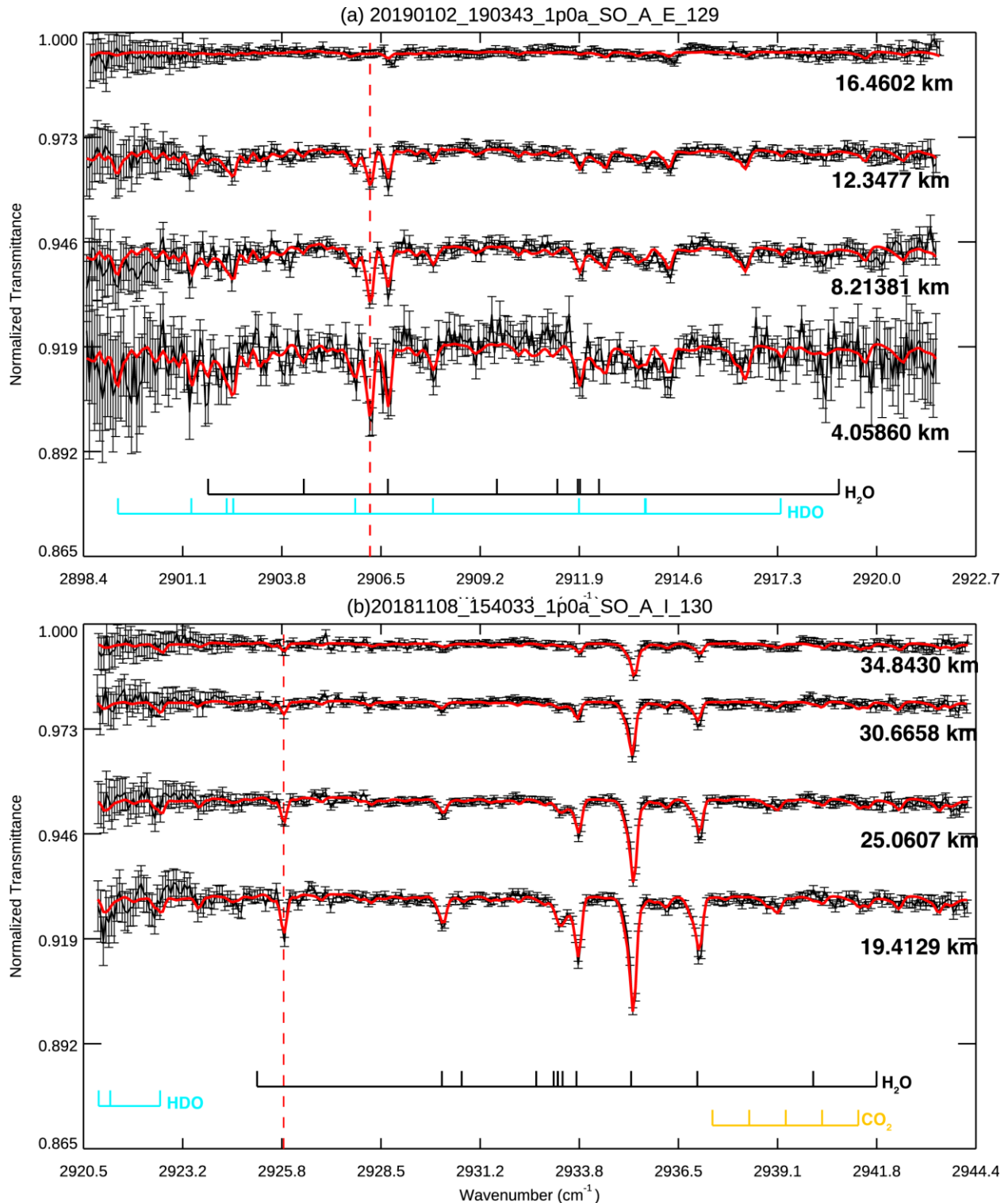
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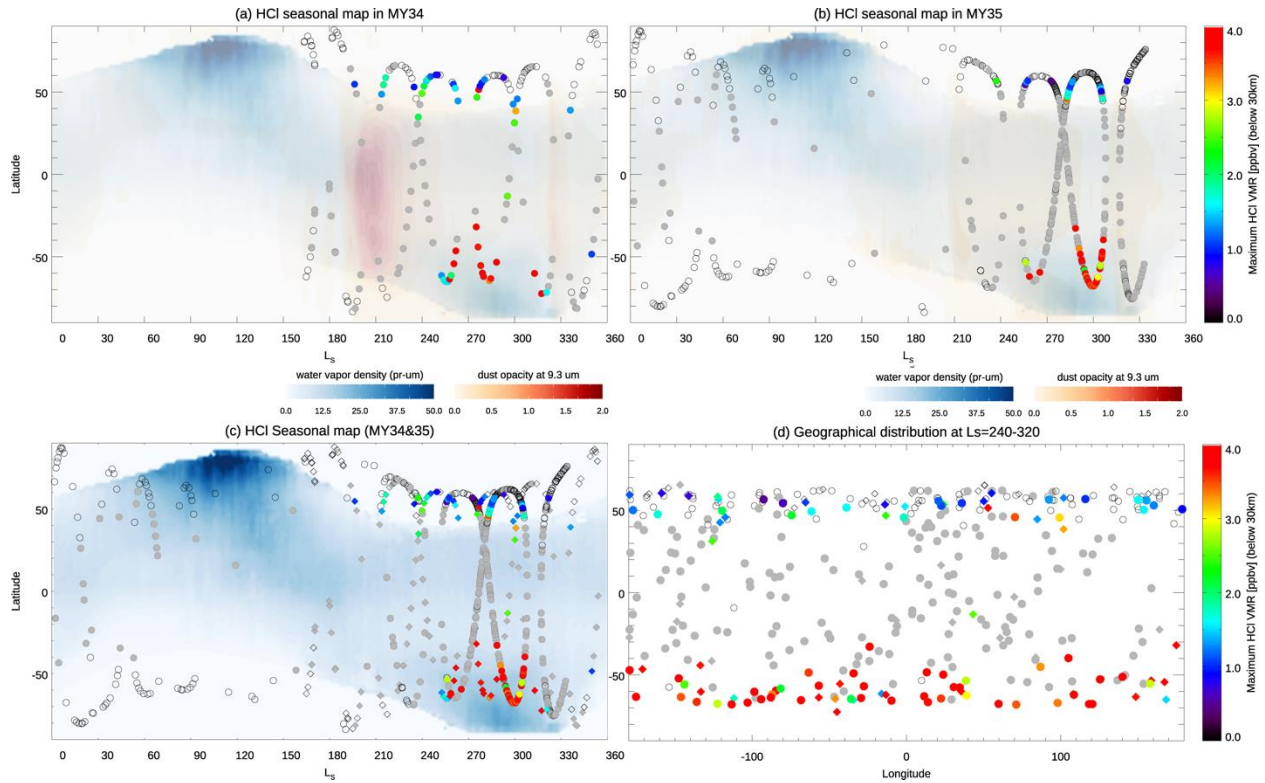
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538 **Figure 1.** Examples of the NOMAD-SO spectra with signatures of HCl: (a) measurements in the
 539 diffraction order 129 performed on 2nd January 2019 ($L_s=317.4^\circ$, Latitude= 72°S ,
 540 Longitude= 46°W); (b) measurements in the diffraction order 130 performed on 8th November
 541 2018 ($L_s=284.5^\circ$, Latitude= 63°S , Longitude= 149°E). The best-fit synthetic spectra are shown by

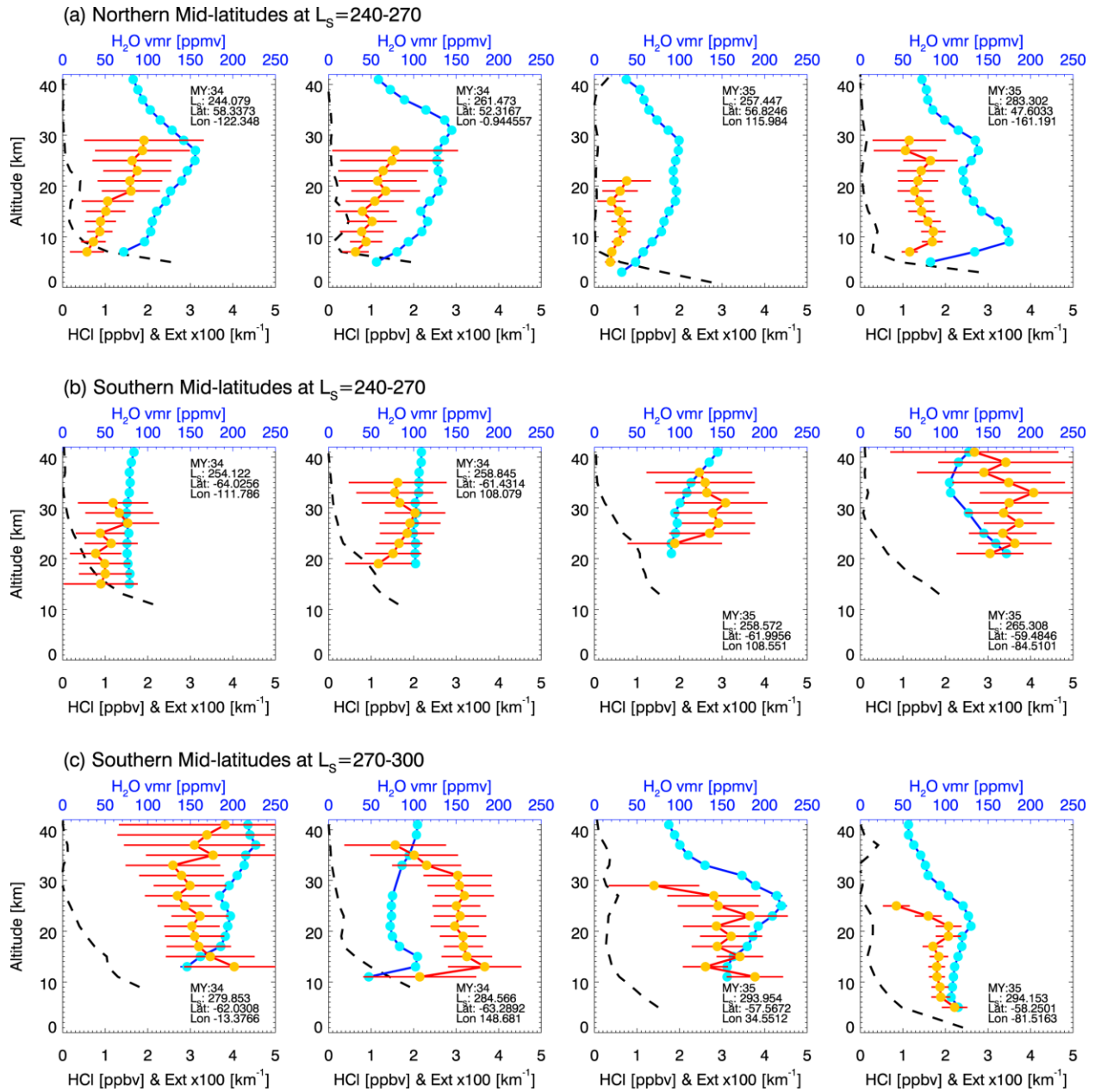
542 the red curves. The vertical dashed lines in red represent the position of the HCl lines. The other
 543 spectral signatures are absorptions due to water vapor and CO₂. The bottom markers show the
 544 position of the strong H₂O ($S > 1 \times 10^{-24}$ cm, black), HDO ($S > 1 \times 10^{-24}$ cm, light blue), and CO₂ (S
 545 $> 1 \times 10^{-28}$ cm, orange) lines in the main diffraction order.

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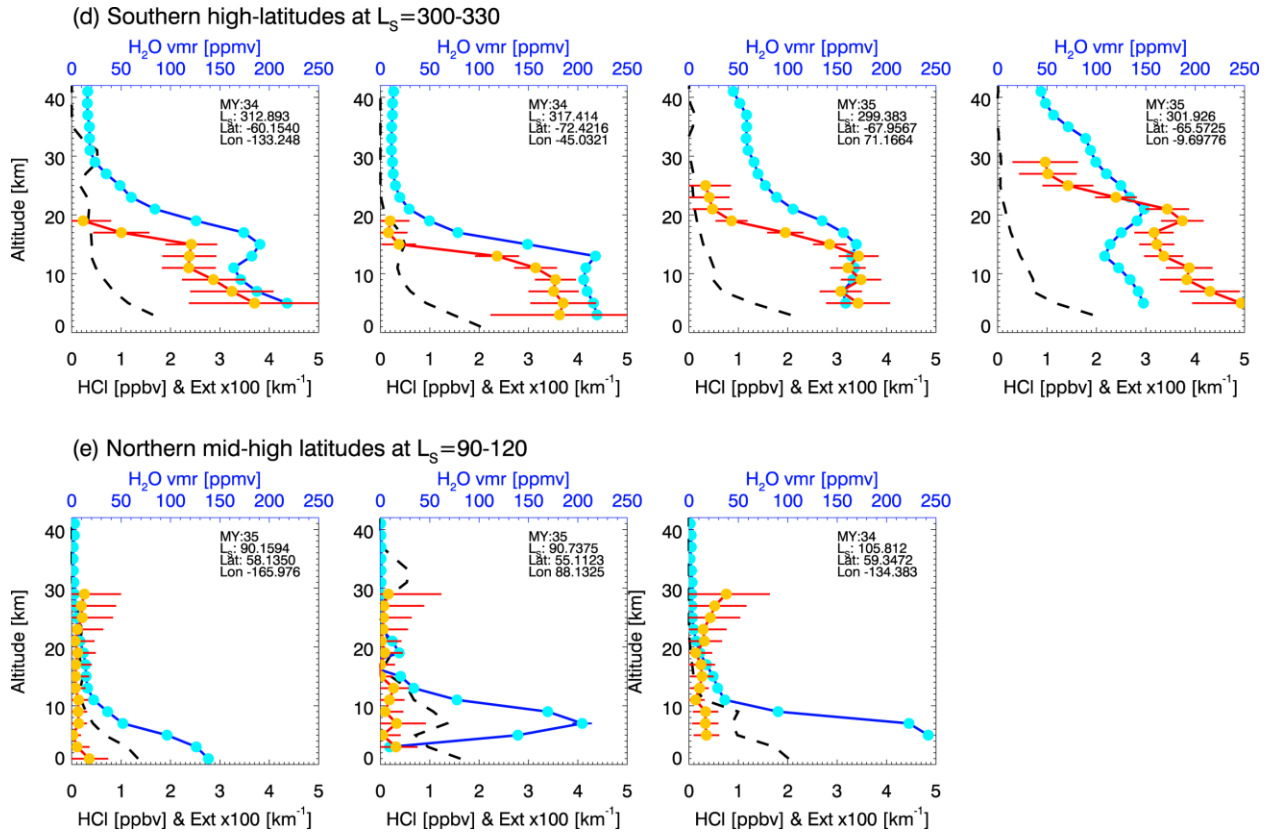
550 **Figure 2.** (a-c) Solar longitude - Latitude map of the maximum HCl mixing ratio (ppbv) below
 551 30 km in (a) MY 34, (b) MY 35, and (c) MY34-35 plotted together. Only 3-σ detections are
 552 shown here. The gray points show observations corresponding to dust top altitude greater than 25
 553 km, for which it is generally difficult to perform robust retrievals. The background color maps
 554 show the column-integrated water vapor density (pr-μm) obtained by MGS/TES for Mars year
 555 26 (Smith, 2002; 2006) and the column-integrated dust opacity at 9.3 μm normalized for 610 Pa
 556 for MY 31 (b) and MY 34 (a) (Montabone et al., 2020). (d) Geographical distribution of HCl
 557 below 30 km in the seasonal range between L_s=240° and 320°.
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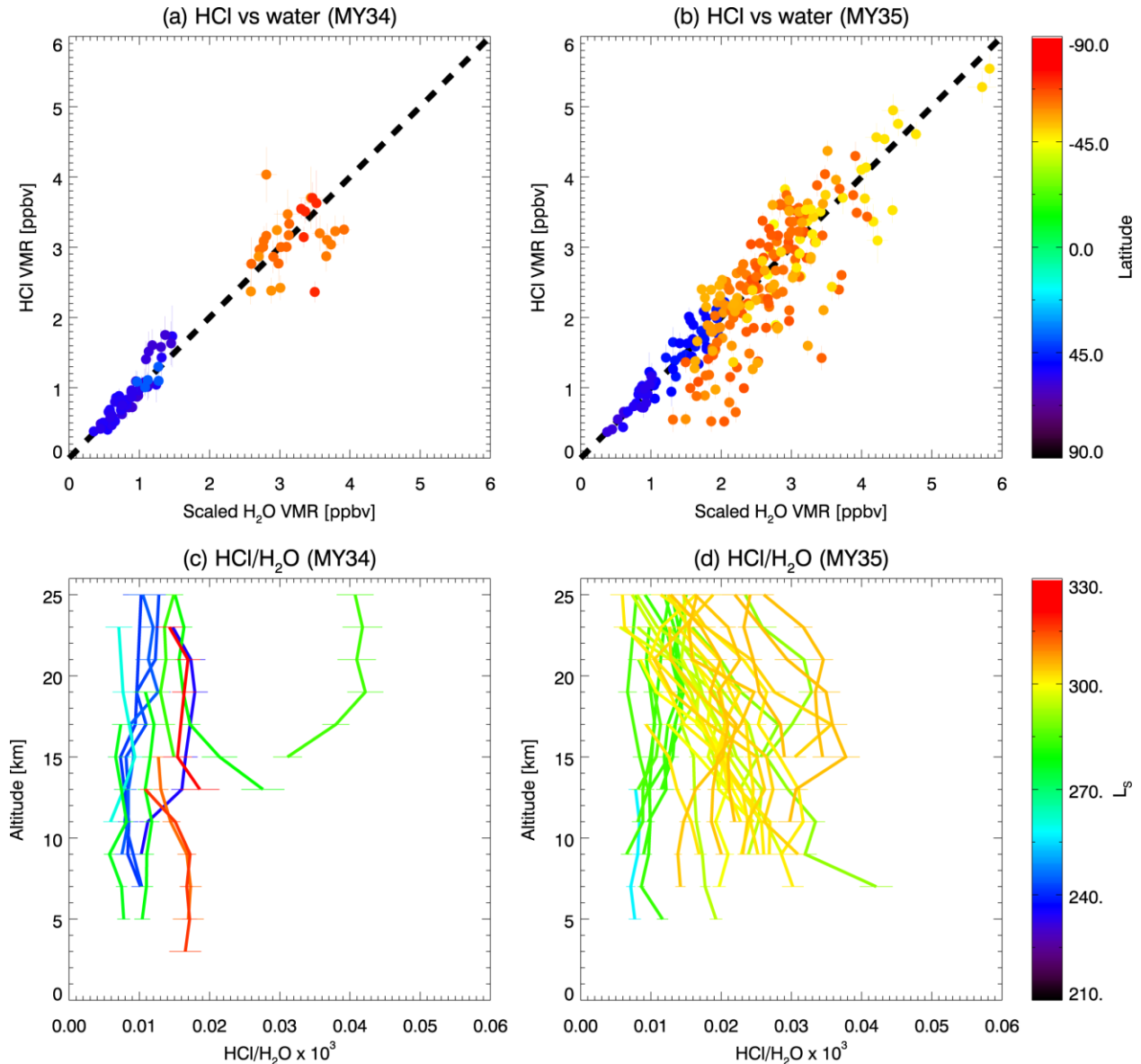


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560 **Figure 3.** Representative vertical profiles of HCl, water vapor, and aerosols extinction at (a) the
 561 northern mid-latitudes ($50^\circ-60^\circ\text{N}$) at $L_s=240^\circ-270^\circ$; (b) the southern high-latitudes ($60^\circ-70^\circ\text{S}$)
 562 during the perihelion ($L_s=240^\circ-270^\circ$); (c) the southern mid-latitudes (30°S and 60°S) at $L_s=270^\circ-$
 563 300° ; (d) the southern high-latitudes ($60^\circ\text{S}-70^\circ\text{S}$) at $L_s=300^\circ-330^\circ$; and (e) the northern mid-
 564 latitudes ($50^\circ-60^\circ\text{N}$) at $L_s=90^\circ-120^\circ$. The red-orange, blue-light blue, and dashed black curves
 565 show HCl volume mixing ratio (0-5 ppbv), water vapor mixing ratio (0-250 ppmv), and
 566 extinction coefficient ($0.00-0.05 \text{ km}^{-1}$) respectively. The error bars represent $3-\sigma$ uncertainty.

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571 **Figure 4.** (a-b) HCl volume mixing ratios are plotted against scaled water vapor mixing ratios,
 572 for all profiles combined (a: MY34, b: MY35). The water vapor mixing ratios are scaled by the
 573 ratio of the HCl and H₂O partial column densities below 25 km within each profile (see SI-1).
 574 When HCl and H₂O profiles are similar in shape, their points will fall on or near the identity line.
 575 The color scale represents the latitude of the observations. (c-d) HCl/H₂O ratio for all profiles.
 576 The color scale represents solar longitude (L_s) of the observations.