

Global-scale distribution of ozone in the remote troposphere from ATom and HIPPO airborne field missions.

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1 **Abstract**

2 Ozone is a key constituent of the troposphere where it drives photochemical
3 processes, impacts air quality, and acts as a climate forcer. Large-scale in situ observations of
4 ozone commensurate with the grid resolution of current Earth system models are necessary to
5 validate model outputs and satellite retrievals. In this paper, we examine measurements from
6 the Atmospheric Tomography (ATom, 4 deployments in 2016–2018) and the HIAPER Pole-
7 to-Pole Observations (HIPPO; 5 deployments in 2009–2011) experiments, two global-scale
8 airborne campaigns covering the Pacific and Atlantic basins.

9 ATom and HIPPO represent the first global-scale, vertically resolved measurements
10 of O₃ distributions throughout the troposphere, with HIPPO sampling the atmosphere over
11 the Pacific and ATom sampling both the Pacific and Atlantic. Given the relatively limited
12 temporal resolution of these two campaigns, we first compare ATom and HIPPO ozone data
13 to longer-term observational records to establish the representativeness of our dataset. We
14 show that these two airborne campaigns captured on average 53, 54, and 38 % of the ozone
15 variability in the marine boundary layer, free troposphere, and upper troposphere/lower
16 stratosphere (UTLS), respectively, at nine well-established ozonesonde sites. Additionally,
17 ATom captured the most frequent ozone concentrations measured by regular commercial
18 aircraft flights in the northern Atlantic UTLS. We then use the repeated vertical profiles from
19 these two campaigns to confirm and extend the existing knowledge ~~global-scale picture~~ of
20 tropospheric ozone spatial and vertical distributions throughout the remote troposphere. We
21 highlight a clear hemispheric gradient, with greater ozone in the northern hemisphere,
22 consistent with greater precursor emissions and consistent with previous modeling and
23 satellite studies. We also show that the ozone distribution below 8 km was similar in the
24 extra-tropics of the Atlantic and Pacific basins, likely due to zonal circulation patterns.
25 However, twice as much ozone was found in the tropical Atlantic than in the tropical Pacific,
26 due to well-documented dynamical patterns transporting continental air masses over the
27 Atlantic. Finally, we show that the seasonal variability of tropospheric ozone over the Pacific
28 and the Atlantic basins is driven year-round by transported continental plumes and
29 photochemistry, and the vertical distribution is driven by photochemistry and mixing with
30 stratospheric air. This new dataset provides additional constraints for global climate and
31 chemistry models to improve our understanding of both ozone production and loss processes
32 in remote regions, as well as the influence of anthropogenic emissions on baseline ozone.

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34

35 **1. Introduction**

36 Tropospheric ozone (O₃) plays a major role in local, regional, and global air quality and
37 significantly influences Earth's radiative budget (IPCC, 2013; Shindell et al., 2012). In addition,
38 O₃ drives tropospheric photochemical processes by controlling hydroxyl radical (OH)
39 abundance, which subsequently controls the lifetime of other pollutants including volatile
40 organic compounds (VOCs), methane, and some stratospheric ozone-depleting substances
41 (Crutzen, 1974; Levy, 1971). Sources of O₃ to the troposphere include downward transport from
42 the stratosphere (Junge, 1962) and photochemical production from precursors such as carbon
43 monoxide (CO), methane (CH₄), and VOCs in the presence of nitrogen oxides (NO_x) from
44 natural or anthropogenic sources (Monks et al., 2009). Tropospheric O₃ sinks include photo-
45 dissociation, chemical reactions, and dry deposition. Owing to its relatively long lifetime (~23
46 days in the troposphere; Young et al., 2013), O₃ can be transported across hemispheric scales. O₃
47 mixing ratios over a region thus depend not only on local and regional sources and sinks, but also
48 on long-range transport. Further, the uneven density of O₃ monitoring locations around the globe
49 leads to significant sampling gaps, especially near developing nations and away from land
50 (Gaudel et al., 2018). The troposphere over the remote oceans is among the least-sampled
51 regions, despite hosting 60–70 % of the global tropospheric O₃ burden (Holmes et al., 2013).

52 Since the early 1980's, several aircraft campaigns have addressed this paucity of remote
53 observations, most notably under the umbrella of the Global Tropospheric Experiment (GTE), a
54 major component of the National Aeronautics and Space Administration (NASA) Tropospheric
55 Chemistry Program (https://eosweb.larc.nasa.gov/project/gte/gte_table). Airborne campaigns
56 have targeted both the Pacific and Atlantic Oceans, providing novel characterization of O₃
57 sources, distribution, and photochemistry in the marine troposphere (Browell et al., 1996a; Davis
58 et al., 1996; Jacob et al., 1996; Pan et al., 2015; Schultz et al., 1999; Singh et al., 1996c) and the
59 low-O₃ tropical Pacific pool (Singh et al., 1996b), the pervasive role of continental outflow on O₃
60 production (Bey et al., 2001; Crawford et al., 1997; Heald et al., 2003; Kondo et al., 2004;
61 Martin et al., 2002; Zhang et al., 2008), and the marked influence of African and South
62 American biomass burning on O₃ production in the Southern Hemisphere (Browell et al., 1996b;
63 Fenn et al., 1999; Mauzerall et al., 1998; Singh et al., 1996a; Thompson et al., 1996).
64 Ozonesondes have been launched from remote sites for more than three decades in some places,
65 and have provided additional constraints on the sources and photochemical balance of

66 tropospheric O₃, including a deep understanding of the vertically-resolved tropospheric O₃
67 climatology in select locations (Derwent et al., 2016; Diab et al., 2004; Jensen et al., 2012; Kley
68 et al., 1996; Liu et al., 2013; Logan, 1985; Logan and Kirchhoff, 1986; Newton et al., 2017;
69 Oltmans et al., 2001; Parrish et al., 2016; Sauvage et al., 2006; Thompson et al., 2012). Spatially-
70 resolved O₃ climatology has been provided by routine sampling by commercial aircraft, but has
71 mostly been limited to the upper troposphere or over continental regions (Clark et al., 2015;
72 Cohen et al., 2018; Logan et al., 2012; Petetin et al., 2016; Sauvage et al., 2006; Thouret et al.,
73 1998; Zbinden et al., 2013), and by satellite observations (Edwards et al., 2003; Fishman et al.,
74 1990, 1991; Hu et al., 2017; Thompson et al., 2017; Wespes et al., 2017; Ziemke et al., 2005,
75 2006, 2017), somewhat tempered by large uncertainties (Tarasick et al., 2019b). Recent
76 overview analyses depict the current understanding of global tropospheric O₃ sources,
77 distribution, and photochemical balance and underscore the insufficiency of observations in the
78 remote free troposphere (Cooper et al., 2014; Gaudel et al., 2018; Tarasick et al., 2019b)
79 necessary to improve the current representation of tropospheric O₃ in global chemical models
80 (Young et al., 2018). Spatial and temporal representativeness of O₃ observations is currently the
81 biggest source of uncertainty when inferring O₃ climatology in the free troposphere, even in
82 regions where observation are abundant but not ideally distributed (Lin et al., 2015b; Tarasick et
83 al., 2019b). Most studies reporting global O₃ distribution use satellite observations (Edwards et
84 al., 2003; Fishman et al., 1990, 1991; Thompson et al., 2017; Wespes et al., 2017; Ziemke et al.,
85 2005, 2006, 2017), modeling analyses (Hu et al., 2017), or observations spatially expanded using
86 back trajectory calculations (e.g., Liu et al., 2013; Tarasick et al., 2010). While useful, these
87 studies come with somewhat large uncertainties, as recently noted by reports from the
88 Tropospheric Ozone Assessment Report (TOAR), and thus require additional in situ observations
89 to be used as a validation bench-mark (Tarasick et al., 2019b; Young et al., 2018).

90 The Atmospheric Tomography mission (ATom, <https://espo.nasa.gov/atom>) was a NASA
91 Earth Venture airborne field project to address the sparseness of atmospheric observations over
92 remote ocean regions by systematically sampling the troposphere over the Pacific and Atlantic
93 basins along a global-scale circuit (Fig. 1). ATom deployed an extensive payload on the NASA
94 DC-8 aircraft, measuring a wide range of chemical, microphysical, and meteorological
95 parameters in repeated vertical profiles from 0.2 km to over 13 km altitude, from the Arctic to
96 the Antarctic over the Pacific and Atlantic Oceans, in four separate seasons from 2016 to 2018.

97 ATom built on a previous study, the HIAPER Pole-to-Pole Observations mission (HIPPO,
98 https://www.eol.ucar.edu/field_projects/hippo). The goal of HIPPO was to measure atmospheric
99 distributions of important greenhouse gases and reactive species over the Pacific Ocean, from the
100 surface to the tropopause, five times during different seasons from 2009 to 2011. Together,
101 ATom and HIPPO provide recent and comprehensive information about the altitudinal,
102 latitudinal, and seasonal composition of the remote troposphere over the Pacific, and over the
103 Atlantic for ATom. In addition, ATom and HIPPO sampling strategies were designed to deliver
104 an objective climatology of key species to enable modelling of air parcel reactivity of the remote
105 troposphere (Prather et al., 2017).

106 Here we use existing ozonesonde and commercial aircraft observations of O₃ at selected
107 locations along the ATom and HIPPO circuits to provide a climatological context for the
108 altitudinal, latitudinal, and seasonal distributions of O₃ derived from the systematic airborne in
109 situ “snapshots”. Long-term O₃ observations are obtained from decades of ozonesonde vertical
110 profiles (e.g., Oltmans et al., 2013; Thompson et al., 2017) and from ~60,000 flights using the
111 In-service Aircraft for a Global Observing System (IAGOS) infrastructure (Petzold et al., 2015;
112 <http://www.iagos.org>). Ozonesondes have typically been launched weekly for two decades or
113 more, depending on the site, and have sampled a wide range of air masses across the globe, from
114 O₃-poor remote surface locations to the O₃-rich stratosphere. IAGOS commercial aircraft have
115 provided daily measurements in the upper troposphere and lower stratosphere (UTLS) for the
116 past 25 years, especially over the northern midlatitudes between America and Europe.
117 Combined, the ozonesonde and IAGOS datasets offer robust measurement-based climatologies
118 that quantify the full expected range of atmospheric O₃ variability with altitude and season.
119 The in-situ data from temporally-limited intensive field studies can be placed in context by
120 comparing them with long-term ozonesonde and commercial aircraft monitoring data. Evaluating
121 the representativeness of in situ observations from airborne campaigns by comparing them to
122 longer-term observational records is a critical exercise never before done at such a global scale.
123 We show that ATom and HIPPO measurements capture the spatial and, in some cases, temporal
124 dependence of O₃ in the remote atmosphere, thus highlighting the usefulness of airborne
125 observations to fill in the gaps of established but limited O₃ climatologies and other similarly
126 long-lived species. Then, we use the geographically extensive ATom and HIPPO vertical profile

127 data to establish a more complete measurement-based benchmark for O₃ abundance and
128 distribution in the remote marine atmosphere.

129

130 **2. Measurements**

131 **2.1 ATom**

132 The four ATom circuits occurred in July–August 2016 (ATom-1), January–February
133 2017 (ATom-2), September–October 2017 (ATom-3), and April–May 2018 (ATom-4), thus
134 spanning all four seasons in both hemispheres over a two-year timeframe (Table S1). The
135 mission in total consisted of 48 science flights and 548 vertical profiles distributed nearly equally
136 along the global circuit. All four deployments completed roughly the same loop, starting and
137 ending in Palmdale, California, USA (Fig. 1). A notable addition during ATom-3 and -4 were
138 out-and-back flights from Punta Arenas, Chile to sample the Antarctic troposphere and UTLS.

139 O₃ was measured using the National Oceanic and Atmospheric Administration (NOAA)
140 nitrogen oxides and ozone (NO_yO₃) instrument. The O₃ channel of the NO_yO₃ instrument is
141 based on the gas-phase chemiluminescence (CL) detection of ambient O₃ with pure NO added as
142 a reagent gas (Ridley et al., 1992; Stedman et al., 1972). Ambient air is continuously sampled
143 from a pressure-building ducted aircraft inlet into the NO_yO₃ instrument at a typical flow rate of
144 1025.0 ± 0.2 standard cubic centimeters per minute (sccm) in flight. Pure NO reagent gas flow
145 delivered at 3.450 ± 0.006 sccm is mixed with sampled air in a pressure (8.00 ± 0.08 Torr) and
146 temperature (24.96 ± 0.01 °C) controlled reaction vessel. NO-induced CL is detected with a dry-
147 ice-cooled, red-sensitive photomultiplier tube and the amplified digitized signal recorded using
148 an 80 MHz counter; pulse coincidence corrections at high count rates were applied, but are
149 negligible for the data presented in this work. The instrument sensitivity for measuring O₃ under
150 these conditions is 3150 ± 80 counts per second per part per billion by volume (ppbv) averaged
151 over the entire ATom circuit. CL detector calibrations were routinely performed both on the
152 ground and during flight by standard addition of O₃ produced by irradiating ultrapure air with
153 185 nm UV light and independently measured using UV optical absorption at 254 nm. All O₃
154 measurements were taken at a temporal resolution of 10 Hz, averaged to 1 Hz, and corrected for
155 the dependence of instrument sensitivity on ambient water vapor content (Ridley et al., 1992).
156 Under these conditions the total estimated 1 Hz uncertainty at sea level is $\pm (0.015 \text{ ppbv} + 2 \%)$.

157 A commercial dual-beam photometer (2B Technologies model 211) based on UV optical
158 absorption at 254 nm also measured O₃ on ATom, with an estimated uncertainty of \pm (1.5 ppbv +
159 1 %) at a 2-second sampling resolution. Comparison of the 2B absorption instrument O₃ data to
160 the NO_yO₃ CL instrument O₃ data agreed to within combined instrumental uncertainties, lending
161 additional confidence to the NO_yO₃ CL instrument calibration. For the ATom project we use
162 NO_yO₃ instrument O₃ data in the following analyses.

163 Data from two CO measurements were combined in this analysis. The Harvard quantum
164 cascade laser spectrometer (QCLS) instrument used a pulsed quantum cascade laser tuned at
165 \sim 2160 cm⁻¹ to measure the absorption of CO through an astigmatic multi-pass sample cell with
166 76 m path length and detection using a liquid-nitrogen-cooled HgCdTe detector (Santoni et al.,
167 2014). In-flight calibrations were conducted with gases traceable to the NOAA World
168 Meteorological Organization (WMO) X2014A scale, and the QCLS observations have an
169 accuracy and precision of 3.5 and 0.15 ppb for 1 Hz data, respectively. CO was also measured by
170 the NOAA cavity ring-down spectrometer (CRDS, Picarro, Inc., model G2401-m; Karion et al.,
171 2013) in the 1.57 μ m region with a total uncertainty of 5.0 ppbv for 1 Hz data. The NOAA
172 Picarro data were also reported on the World Meteorological Organization (WMO) X2014A
173 scale. The combined CO data (CO-X) used here corresponds to the QCLS data, with the Picarro
174 measurement used to fill calibration gaps in the QCLS time series.

175 Water (H₂O) vapor was measured using the NASA Langley Diode Laser Hygrometer
176 (DLH), an open-path infrared absorption spectrometer that uses a laser locked to a water vapor
177 absorption feature at \sim 1.395 μ m. Raw data are processed at the instrument's native \sim 100 Hz
178 acquisition rate and averaged to 1 Hz with an overall measurement accuracy within 5 %.

179

180 2.2 HIPPO

181 The HIPPO mission consisted of five seasonal deployments over the Pacific basin
182 between 2009 and 2011, from the North Pole to the coastal waters of Antarctica (Wofsy, 2011).
183 HIPPO deployments consisted of two transects, southbound and northbound, and occurred in
184 January 2009 (HIPPO-1), October–November 2009 (HIPPO-2), March–April 2010 (HIPPO-3),
185 June–July 2011 (HIPPO-4) and August–September 2011 (HIPPO-5). The platform used was the
186 NSF Gulfstream V (GV) aircraft. More details can be found in Table S1.

187 A NOAA custom-built dual-beam photometer based on UV optical absorption at 254 nm
188 was used to measure O₃ (Proffitt and McLaughlin, 1983). The uncertainty of the 1 Hz O₃ data is
189 estimated to be $\pm (1 \text{ ppbv} + 5 \%)$ for 1 Hz data. A commercial dual-beam O₃ photometer (2B
190 Technologies model 205) based on UV optical absorption at 254 nm was also included in the
191 HIPPO payload. Comparison of the 2B O₃ data to the NOAA O₃ data showed general agreement
192 within combined instrument uncertainties on level flight legs. For the HIPPO project we use
193 NOAA O₃ data in the following analyses.

194 Data from two CO measurements were combined in this analysis. The QCLS instrument
195 was the same instrument as used during ATom and described in section 2.1. CO was also
196 measured by an Aero-Laser AL5002 instrument using vacuum UV resonance fluorescence (in
197 the 170–200 nm range) instrument with an uncertainty of $\pm (2 \text{ ppbv} + 3 \%)$ at a 2-second
198 sampling resolution. The combined CO data (CO-X) used here corresponds to the QCLS data,
199 with the Aero-Laser measurement used to fill calibration gaps in the QCLS time series.

200

201 2.3 IAGOS

202 IAGOS is a European Research Infrastructure that provides airborne in situ chemical,
203 aerosol, and meteorological measurements using commercial aircraft (Petzold et al., 2015). The
204 IAGOS Research Infrastructure includes data from both the CARIBIC (Civil Aircraft for the
205 Regular Investigation of the atmosphere Based on an Instrument Container; Brenninkmeijer et
206 al., 2007) and MOZAIC (Measurements of OZone and water vapor by Airbus In-service
207 airCraft; Marenco et al., 1998) programs, providing measurements from ~60,000 flights since
208 1994. We note the relative lack of IAGOS data over the Pacific compared to the Atlantic (shorter
209 temporal record, lower flight frequency, and much fewer flights with concomitant O₃ and CO
210 measurements), and therefore limited the comparison to the Atlantic. Because commercial
211 aircraft cruise altitudes over the ocean are predominantly between 9 and 12 km, the comparison
212 between ATom and IAGOS is further limited to the UTLS (Fig. 1). More details are shown in
213 Table S1.

214 Identical dual-beam UV absorption photometers measured O₃ aboard the IAGOS flights.
215 An instrument comparison demonstrated that the photometers (standard model 49, Thermo
216 Scientific, modified for aircraft use) showed good consistency in measuring O₃ following an

217 inter-comparison experiment (Nédélec et al., 2015). The associated uncertainty is $\pm (2 \text{ ppbv} + 2$
218 $\%)$ at a 4-second sampling resolution (Thouret et al., 1998).

219 CO measurements were made using infra-red absorption photometers (standard model 48
220 Trace Level, Thermo Scientific, modified for aircraft use) with an uncertainty of $\pm (5 \text{ ppbv} + 5$
221 $\%)$ at a 30-second sampling resolution (Nédélec et al., 2003, 2015).

222

223 2.4 Ozonesondes

224 Ozonesondes have measured the vertical distribution of O₃ in the atmosphere for decades,
225 and provide some of the longest tropospheric records that are commonly used to determine
226 regional O₃ trends (Gaudel et al., 2018; Leonard et al., 2017; Oltmans et al., 2001; Tarasick et
227 al., 2019a; Thompson et al., 2017). Ozonesonde launching sites are operated by the NOAA
228 ESRL Global Monitoring Division (GMD), NASA Goddard's Southern Hemisphere Additional
229 OZonesondes (SHADOZ) program, the New Zealand National Institute of Water & Atmospheric
230 Research (NIWA), the National Meteorological Center of Argentina (SNMA) in collaboration
231 with the Finnish Meteorological Institute (FMI), or Environment and Climate Change Canada. A
232 more detailed description of each ozonesonde site and corresponding dataset can be found in
233 Tables S1 and S2. All sites use electrochemical concentration cell (ECC) ozonesondes that rely
234 on the potassium iodide electrochemical detection of O₃, and which provide a vertical resolution
235 of about 100 m (Komhyr, 1969). The associated uncertainty is usually $\pm (5\text{--}10 \%)$ (Tarasick et
236 al., 2019b; Thompson et al., 2019; Witte et al., 2018).

237

238 2.5 Data analysis

239 In this analysis, ATom flight tracks were divided into the Atlantic and Pacific basins, and
240 further subdivided into five regions within those basins: tropics, and northern and southern
241 middle- and high-latitudes. Vertical profiles presented graphically in this paper show O₃ median
242 values and the 25th to 75th percentile range within the 0–12 km tropospheric column sampled by
243 the DC-8 aircraft. These medians were obtained by averaging with equal weight the individual
244 profiles within each region over 1 km altitude bins.

245 HIPPO flight tracks are illustrated in Figure 1. The flight segments used for comparison
246 with ATom were binned into the same Pacific latitude and longitude bands as for ATom. HIPPO
247 vertical profile data are derived using the same methodology as for ATom.

248 All IAGOS flight tracks over the northern and tropical Atlantic are represented in Figure
249 1 in green. The latitude bands used to parse IAGOS data are consistent with the ones used for
250 ATom. The longitude bands are 50° W to 20° W in the tropics, 50° W to 10° W in the northern
251 midlatitudes, and 110° W to 10° W in the northern high-latitudes. Variations of the longitude
252 band widths do not significantly affect the O₃ distributions measured by IAGOS. Data from all
253 flights from 1994 to 2017 were included in the IAGOS dataset considered here, and were then
254 divided into two altitude bins (8–10 km and 10–12 km) in order to better understand the
255 influence of different O₃ sources (e.g., anthropogenic, stratospheric) on these two layers of the
256 atmosphere.

257 We compare the ozonesonde measurements to ATom and HIPPO aircraft data sampled
258 within 500 km of each ozonesonde launching site, since we expect a robust correlation in the free
259 troposphere within this distance (Liu et al., 2009). We used the surface coordinates of the
260 ozonesonde sites because the in-flight coordinates of ozonesondes are not available at all sites.
261 For comparison with ozonesonde long term records, we consider three regions of the
262 atmosphere: boundary layer (0–2 km), free troposphere (2–8 km), and UTLS (8–12 km). For
263 each layer, we compared monthly O₃ distributions from ozonesondes with the corresponding
264 seasonal O₃ distributions from aircraft measurements using the skill score (S_{score}) metric (Perkins
265 et al., 2007). The S_{score} is calculated by summing the minimum probability of two normalized
266 distributions at each bin center, and therefore measures the overlapping area between two
267 probability distribution functions. If the distributions are identical, the skill score will equal 100
268 % (see Fig. S1 for further examples). Note the S_{score} is positively correlated with the size of the
269 bin used to compare distributions. Here we chose a bin size of 5 ppbv, which is larger than the
270 combined precision of ATom, HIPPO, and IAGOS measurements, but small enough to separate
271 distinct air masses and their influence on O₃ distribution. Variables such as the distance to each
272 ozonesonde launching site (500 km in this study), the bin size of the O₃ distributions (5 ppbv in
273 this study), and the length of each ozonesonde record (full length in this study) can shift the
274 vertically-averaged S_{score} value by up to 8 % (Table S3). We therefore treat this 8 % as a rough
275 estimate of the precision of the S_{score} values presented here.

276 All three techniques (chemiluminescence, UV absorption, and ECC) used to measure O₃
277 for the datasets analyzed in this work have been shown to provide directly-comparable accurate
278 measurements with well-defined uncertainties (Tarasick et al., 2019b).

279

280 2.6 Back trajectory analysis

281 Analysis of back trajectories for air masses sampled during airborne missions is useful to
282 examine the air mass source regions and causes for O₃ variability over the Pacific and Atlantic
283 Oceans. We calculated ten-day back trajectories using the Traj3D model (Bowman, 1993;
284 Bowman and Carrie, 2002) and National Centers for Environmental Prediction (NCEP) global
285 forecast system (GFS) meteorology. Trajectories were initialized each minute along all of the
286 ATom flight tracks.

287

288 **3. Comparison of ATom and HIPPO O₃ distributions to longer-term observational** 289 **records**

290 Here we use existing ozonesonde and IAGOS observations of O₃ at selected locations
291 along the ATom and HIPPO circuits to provide a climatological context for O₃ distributions
292 derived from the systematic airborne in situ “snapshots”. We quantify how much of O₃
293 variability, occurring on timescales ranging from hours to decades, was captured by the
294 temporally-limited HIPPO and ATom missions.

295

296 3.1. Comparison to ozonesondes

297 ATom and HIPPO explored the fidelity with which airborne missions represent O₃
298 climatology in the remote troposphere. Here, we show that aircraft-measured median O₃ follows
299 the seasonal ozonesonde-measured median O₃ cycle at most of the sites studied here, and at
300 almost all altitudes – with a few exceptions (Figs. 2 and 3). Figure 2 plots the monthly median O₃
301 measurements from the tropical ozonesonde sites in three altitude bins, along with the median
302 values obtained from HIPPO and ATom measurements. Figure 3 plots the same for the
303 extratropical sites. Figure 4 correlates the median O₃ measured by aircraft in Figures 2 and 3
304 with those measured by ozonesondes. At the Eureka site, the winter and spring ATom
305 deployments recorded a significantly lower median O₃ compared to the corresponding
306 ozonesonde monthly median O₃ in the 0–2 km range (Fig. 3). Eureka is frequently subject to
307 springtime O₃ depletion events at the surface due to atmospheric bromine chemistry, which is
308 well recorded by the ozonesonde record (Fig. 3; Tarasick and Bottenheim, 2002). Sampling
309 during O₃ depletion events significantly lowered the ATom winter and springtime O₃

310 distributions near this site. In the 2–8 km range, there is a very good seasonal agreement between
311 ATom/HIPPO and the ozonesondes (Fig. 4b). Most seasonal differences are found above 8 km
312 (e.g., ATom in February at Trinidad Head and in May at Eureka; Fig. 3) and can be linked to the
313 occurrence – or absence – of stratospheric air sampling during ATom and HIPPO. In the absence
314 of stratospheric air mixing (< 8 km in Fig. 4), ATom/HIPPO successfully capture a large fraction
315 of O₃ climatology everywhere (Figs. 4b and 4c).

316
317 Figures 5 and 6 show vertical profiles of O₃ distributions by season at each ozonesonde
318 site, along with comparisons to HIPPO and ATom vertical profiles. Our analysis reveals that O₃
319 distributions derived from the ATom and HIPPO seasonal “snapshots” capture 30–71 % of the 1
320 km-vertically binned O₃ distribution established by long-term ozonesonde climatologies. For the
321 nine ozonesonde sites considered here, ATom and HIPPO captured on average 53 %, 54 %, and
322 38 % of the O₃ distribution in the 0–2 km, 2–8 km, and 8–12 km altitude bins, respectively.

323 Larger differences between ATom/HIPPO and the ozonesonde records in the UTLS (8–
324 12 km) can be ascribed to O₃ variability from stratospheric–tropospheric exchange, which is not
325 always captured by the ATom and HIPPO missions. This increased O₃ variability in the UTLS is
326 well-described by the long term ozonesonde records at Lauder, Trinidad Head, Eureka, Ushuaia,
327 and Marambio (Figs. 3 and 6). In these middle- and high-latitude locations in both hemispheres,
328 O₃ variability is especially pronounced during winter and spring, time periods favorable to more
329 frequent stratospheric air mixing (Greenslade et al., 2017; Lin et al., 2015a; Tarasick et al.,
330 2019a). Furthermore, the probability of sampling stratospheric air masses at ATom and HIPPO
331 ceiling altitude (12–14 km) increases with latitude, resulting in a lower S_{score} between the
332 ATom/HIPPO and ozonesonde datasets at the extra-tropical sites than at the tropical sites (Figs.
333 S2a and S2b).

334 In the boundary layer (0–2 km) of the remote troposphere, O₃ variability is predominantly
335 impacted by loss mechanisms. Ozonesonde records show instances of O₃ mixing ratios lower
336 than 10 ppbv throughout the year in the boundary layer at the nine sites studied here (Figs. 2 and
337 3). The lowest O₃ mixing ratios are a result of (a) photochemical destruction over the oceans in
338 the tropics (Monks et al., 1998, 2000; Thompson et al., 1993), (b) O₃-destroying halogen
339 emissions in polar regions in springtime (e.g., Fan and Jacob, 1992), and (c) transport of O₃-poor
340 oceanic air over the midlatitude sites (e.g., Neuman et al., 2012).

341 ATom and HIPPO best describe the O₃ distribution in the free troposphere (2–8 km; Figs.
342 S2a and S2b). This suggests that airborne campaigns can capture global baseline O₃ values,
343 along with the long-range transport of O₃ pollution plumes often lofted to this altitude range and
344 responsible for O₃ variability.

345
346 While ATom consisted of one transect per ocean per season, HIPPO covered the Pacific
347 twice per seasonal deployment (southbound and northbound). The 1 km-binned S_{score} is on
348 average higher when two combined seasonal HIPPO flights (southbound and northbound) were
349 available to compare to ozonesonde records, as opposed to when comparing O₃ profiles from
350 individual HIPPO transects with ozonesonde records (Fig. S2c). In addition, two seasonal flights
351 during HIPPO reduced the occurrence of low S_{score} values. This S_{score} decrease from flying only
352 one Pacific transect only during ATom was traded for the increase of vertical profiles over the
353 Atlantic Basin, which was not sampled during HIPPO. Future airborne missions with multiple
354 seasonal vertical profiles over large-scale regions would be ideal to better depict the full range of
355 tropospheric O₃ variability.

356

357 3.2. Comparison to IAGOS

358 IAGOS O₃ and CO observations in the northern Atlantic UTLS provide a measurement-
359 based climatology at commercial aircraft cruise altitudes for comparison to ATom. Simultaneous
360 measurements of O₃ and CO are of particular interest because CO provides a long-lived tracer of
361 continental emissions, which helps to differentiate O₃ sources (Cohen et al., 2018). We note that
362 while IAGOS measurements encompass hundreds of seasonal flights (depending on the region),
363 ATom sampled within each latitude band and season on one or two flights only (Fig. 1). Thus,
364 variability in the UT that occurred on timescales longer than a day was not captured by ATom.
365 Consequently, it is not surprising to see that ATom systematically under-sampled tropospheric
366 O₃ (and CO) variability compared to IAGOS at all latitudes in the northern Atlantic (Figs. 7 and
367 8). ATom captured on average 40 % of the O₃ variability measured by IAGOS in the Atlantic
368 UTLS (Fig. 7), on par with the S_{score} of 38 % obtained when comparing ATom and HIPPO to
369 ozonesonde data (see section 3.1).

370

371 In the middle- and high-latitudes, the shapes of the O₃ vs. CO scatterplots from IAGOS
372 data demonstrate that distinct sources contribute to O₃ levels in the UTLS (Figs. 8a and 8b;
373 Gaudel et al., 2015). The high O₃ (>150 ppbv) – low CO (<100 ppbv) range corresponds to
374 intrusions of stratospheric air, which were mostly sampled in the spring season during ATom,
375 supporting previous observations of increased stratospheric air mixing during this season (Lin et
376 al., 2015a; Tarasick et al., 2019a). The low O₃ (<50 ppbv) – low CO (<100 ppbv) range
377 corresponds to the tropospheric baseline air, whereas the intermediate O₃ (50–120 ppbv) – high
378 CO (>100 ppbv) range generally represents the influence of air masses transported from
379 continental regions. During ATom, high O₃ and low CO in the middle- and high-latitude UTLS
380 were typical of stratospheric and baseline tropospheric air mixing.

381
382 O₃ measured during IAGOS rarely exceeds 150 ppbv in the northern tropical Atlantic
383 UTLS (Fig. 8c). This is expected because the tropical tropopause is typically situated between 13
384 and 17 km altitude and IAGOS flights typically cruise below 12 km. Therefore, instances of
385 stratospheric intrusions at IAGOS flight altitudes are limited. O₃ measured during ATom in the
386 tropical Atlantic above 8 km was generally positively correlated with CO, showing the
387 contribution of tropospheric O₃ production from continental sources reaching high altitudes.
388 Given this variability, the ATom data do not capture the extrema of UTLS O₃ variability in the
389 IAGOS measurements (Figs. 7 and 8). However, the most frequently measured O₃ and CO
390 values from ATom overlap with the most frequently measured O₃ and CO values from IAGOS
391 (contours in Fig. 8), suggesting that ATom captured the mode of the O₃ and CO distributions
392 from IAGOS in the northern Atlantic UTLS.

393

394 **4. O₃ distributions in the remote troposphere from ATom and HIPPO**

395 We have established the fidelity of ATom and HIPPO O₃ data by comparison to
396 measurement-based climatologies of tropospheric O₃ from well-established ozonesonde and
397 commercial aircraft monitoring programs. In the following sections we exploit the systematic
398 nature of the ATom and HIPPO vertical profiles to provide a global-scale picture of tropospheric
399 O₃ distributions in the remote atmosphere. Figure 9 presents the altitudinal, latitudinal, and
400 seasonal distribution of tropospheric O₃ during ATom and HIPPO. Higher O₃ was measured
401 during ATom & HIPPO in the Northern Hemisphere (NH) than in the Southern Hemisphere

402 (SH), both in the Pacific and in the Atlantic. This distribution gradient has previously been
403 shown by global O₃ mapping from modeling, satellite, and ozonesonde analyses (e.g., Hu et al.,
404 2017; Liu et al., 2013). This finding holds true throughout the tropospheric column from 0 to 8
405 km, both in the middle- and high-latitudes (Fig. S3). In the midlatitudes below 8 km, median O₃
406 ranged between 25 and 45 ppbv in the SH, and between 35 and 65 ppbv in the NH. In the high
407 latitudes below 8 km, median O₃ ranged between 30 and 45 ppbv in the SH, and between 40 and
408 75 ppbv in the NH. Notable features in the global O₃ distribution are discussed in more detail in
409 the following sections. Figure 10 presents the vertically-resolved distribution of tropospheric O₃
410 from 0–12 km for the Atlantic (ATom in green) and for the Pacific (ATom in pink, HIPPO in
411 blue). *S_{score}* values resulting from the comparison of HIPPO and ATom Pacific distributions are
412 shown with blue diamonds, and from the comparison of ATom Atlantic and Pacific distributions
413 with pink squares. Figure 11 is derived from Figure 10 and gives the *S_{score}* values against altitude
414 in the first panel, as well as the relative difference of median O₃ from 0 to 8 km in the second
415 panel.

416

417 4.1. Tropics

418 **Vertical distribution.** O₃ is at a minimum in the tropical marine boundary layer (MBL),
419 especially over the Pacific (Fig. 10a). The lowest measured O₃ in this region was 5.4 ppbv in
420 May during ATom, and 3.5 ppbv in January during HIPPO. The tropical MBL is a net O₃ sink
421 owing to very slow O₃ production rates – NO levels averaged 22 ± 12 pptv in the Pacific and
422 Atlantic MBL during ATom – and rapid photochemical destruction rates of O₃ in a sunny, humid
423 environment (Kley et al., 1996; Parrish et al., 2016; Thompson et al., 1993). Deep stratospheric
424 intrusions into the Pacific MBL were not observed in ATom or HIPPO, in contrast to reports
425 from previous studies (e.g., Cooper et al., 2005; Nath et al., 2016). In the tropics, marine
426 convection within the intertropical convergence zone (ITCZ) is associated with relatively low O₃
427 values throughout the tropospheric column, with median O₃ mixing ratios less than 25 ppbv
428 below 4 km altitude in the tropical Pacific (Fig. 10a; Oltmans et al., 2001). The relative
429 difference between ATom Atlantic and Pacific median O₃ in the tropics below 8 km is
430 consistently higher than a factor of 1.5, with an average *S_{score}* of 43 % (Figs. 10a and 11b). We
431 ascribe this difference to O₃ production from biomass burning (BB) emissions in the continental
432 regions surrounding the tropical Atlantic; back trajectories from the ATom flight tracks show the

433 tropical Atlantic is strongly affected by transport from BB source regions in both Africa and
434 South America (Fig. S4; Jensen et al., 2012; Sauvage et al., 2006; Stauffer et al., 2018;
435 Thompson et al., 2000). In addition, the positive correlation of O₃ enhancements with black
436 carbon (Katich et al., 2018) and reactive nitrogen species (Thompson et al., personal
437 communication) also indicate BB influence. Although ATom and HIPPO data show evidence for
438 extensive and widespread BB influence on O₃ in the Pacific as well, O₃ mixing ratios are
439 consistently more elevated throughout the tropospheric column in the Atlantic. One reason is
440 closer proximity of the mid-ocean Atlantic flight tracks to O₃ precursor source regions. These
441 findings confirm studies that previously highlighted the impact of African BB emissions on O₃
442 production in the tropical Atlantic (e.g., Andreae et al., 1994; Fishman et al., 1996; Jourdain et
443 al., 2007; Williams et al., 2010). Lightning NO_x also play a role in the buildup of O₃ over the
444 tropical Atlantic at certain times of year (Moxim and Levy, 2000; Pickering et al., 1996).

445 **Seasonality.** The seasonal variation of vertical profiles of O₃ in the tropics is lower
446 throughout the column compared to the extra-tropics (Fig. 12), in part due to less stratospheric
447 influence at the highest tropical altitudes. The remoteness of the tropical Pacific flight paths from
448 continental pollution sources also drives the lower seasonal variability here compared to the
449 tropical Atlantic, where BB influence peaks in June–August and October–November,
450 characterized by high O₃ (> 75 ppbv) and high CO (>100 ppbv) (Fig. 13f), significantly
451 increasing the O₃ vertical distribution compared to the other seasons (Figs. 12c, 12h, and 12m).
452 Finally, photochemistry, which regulates O₃ net balance in the troposphere, is less seasonally
453 variable in the tropics than in the extra-tropics, where the photolysis frequency of O₃ ($j(\text{O}_3)$) and
454 photochemical production of O₃ fluctuate annually with solar zenith angle.

455 **O₃ minima and maxima.** Coincident O₃ and CO enhancements were observed in the
456 tropical Atlantic for each ATom circuit (Figs. 9 and 13f), suggesting a year-round influence of
457 continental emissions and distinctive dynamics in this region (Krishnamurti et al., 1996;
458 Thompson et al., 1996). In the tropical Pacific, the April–May period stands out due to an O₃ and
459 CO enhancement episode during HIPPO (Fig. 9) that was attributed to the transport of
460 anthropogenic and BB emissions from southeast Asia (Shen et al., 2014). Deep convection in the
461 tropics brings O₃-poor (<15 ppbv) air to the upper troposphere (Kley et al., 1996; Pan et al.,
462 2015; Solomon et al., 2005). However, the spatial extent of these events remains poorly
463 constrained. Results from ATom and HIPPO suggest that deep convection can loft O₃-poor air at

464 least up to 12 km (the altitude ceiling of this study) in the tropical Pacific, and occurred more
465 frequently between January and May (Figs. 12c and h). During the rest of the year, O₃-poor air
466 was typically confined below 4 km. Conversely, O₃-poor air is confined to the first 2 km in the
467 tropical Atlantic (Fig. S5). Meteorological analysis of tropical ozonesondes shows that
468 subsidence of higher-O₃ air aloft over the Atlantic is one reason O₃-poor air is found only in the
469 boundary layer (Thompson et al., 2000, 2012).

470

471 4.2. Middle- and high-latitudes

472 **Vertical distribution.** In the middle- and high-latitudes, tropospheric O₃ was generally at
473 a minimum in the MBL and increased with altitude. Above 8 km, increasing O₃ with altitude
474 (Figs. 10b–e) and its persistent anticorrelation with CO (Fig. 13) points to stratospheric air
475 sampling as the cause for higher O₃ variability in the extra-tropical UTLS, especially at high
476 latitudes where the tropopause is lower and wave breaking of the polar jet streams can lead to
477 stratospheric intrusions. As a result, the S_{score} decrease above 8 km, summarized in Figure 11a, is
478 ascribed to variability in the influence of stratospheric air. ATom detected little change in the O₃
479 distribution over the Pacific Ocean since HIPPO, with a S_{score} averaging 74 % in the 0–8 km
480 range. The relative difference between median O₃ values from HIPPO and ATom in the Pacific
481 is generally lower than 20 % (Fig. 11b). Similarly, the relative difference between median O₃
482 mixing ratios between ATom Atlantic and Pacific below 8 km is consistently lower than 20 %,
483 with an average S_{score} of 75 % (Fig. 11b). The southern high-latitudes are the only region where
484 the S_{score} below 8 km occasionally fell below 60 % (Fig. 10e). However, a lower S_{score} was
485 expected there as the Atlantic vertical profile is based on only two seasonal flights to Antarctica,
486 whereas there were four seasonal flights in the Pacific. Additionally, HIPPO was less spatially
487 extensive – resulting in fewer data points – in this latitude bin compared to ATom (Fig. 1), which
488 could explain the low S_{score} values when comparing the two missions (Fig. 10e). Nevertheless,
489 the similar O₃ distribution in the extra-tropical free troposphere above the two oceans is
490 consistent with an O₃ lifetime sufficiently long for rapid zonal transport to smooth out variations
491 in baseline O₃ distribution in the remote troposphere, across a relatively wide range of longitudes
492 (Figs. 10b–e). The comparison of O₃ seasonal cycles at remote ozonesonde launching sites of the
493 northern midlatitudes yields similar results and further supports this conclusion (Logan, 1985;
494 Parrish et al., 2020). However, the similarity of the O₃ distribution in the extra-tropical free

495 troposphere above the Atlantic and Pacific is not always evident in satellite-, modelling-, or
496 ozonesonde-derived maps (Gaudel et al., 2018; Hu et al., 2017; Ziemke et al., 2017).
497 Additionally, studies of the spatial representativeness of tropospheric O₃ monitoring networks
498 have also concluded that tropospheric O₃ distributions varied significantly with longitude,
499 especially in the northern middle- and high-latitudes over continents (Liu et al., 2013; Tilmes et
500 al., 2012). In contrast, the ATom findings stem from O₃ measurements predominantly over the
501 oceans, which likely reveal a different picture of O₃ longitudinal distribution away from regional
502 precursor emissions.

503 **Seasonality.** The extra-tropical vertical profiles of O₃ vary seasonally during ATom and
504 HIPPO. The summer season in the middle- and high-latitudes was remarkable over both oceans
505 and hemispheres for the steep O₃ gradients in the tropospheric column (Fig. 12 in black). In the
506 MBL, median O₃ was consistently under 25 ppbv in the summer, whereas O₃ was over 25 ppbv
507 in other seasons. Low O₃ in the MBL in summer reflects the enhanced O₃ photochemical
508 destruction in this NO_x-limited region. Photochemical destruction decreases in dry air in the
509 upper troposphere, thus leading to the steep O₃ gradients observed here. The summer O₃
510 minimum was especially apparent in the high latitudes of the southern Pacific during ATom and
511 extended well above the MBL into the free troposphere (Fig. 12 in black). O₃ mixing ratios were
512 highest in the tropospheric column during springtime in both hemispheres, and over both oceans
513 (Fig. 12 in gold). A notable exception occurred during springtime in the high latitudes of the NH,
514 where several O₃ depletion events were sampled in the lower legs of the Arctic transit. During
515 these events, O₃ mixing ratios lower than 10 ppbv were measured, resulting in a lower 25th
516 percentile of O₃ distribution at the lowest altitude compared to the other seasons (Figs. 12e and
517 12o in gold). A tropospheric O₃ springtime maximum has often been reported in the NH (e.g.,
518 Monks, 2000) when meteorology favors efficient transport of O₃ and precursors from continental
519 air from North America and Eurasia (Owen et al., 2006; Zhang et al., 2017, 2008). Another
520 contributing factor is the increased frequency of stratospheric air mixing in spring that
521 significantly contributes to higher O₃ levels (Lin et al., 2015a; Tarasick et al., 2019a). Further,
522 the tropospheric O₃ springtime maximum in the SH is often attributed to BB emissions reaching
523 a peak (Fishman et al., 1991; Gaudel et al., 2018), but stratospheric air mixing also occurs (Diab
524 et al., 1996, 2004; Greenslade et al., 2017). Here, the O₃/CO relationship in spring shows that the
525 enhanced stratospheric mixing with tropospheric air during this season, both in the northern and

526 southern middle- and high-latitudes, contributes to the increase in column O₃ (Fig. 13). Fall and
527 winter seasons shared similar features in the middle- and high-latitudes: no strong O₃ gradient
528 was measured in the free troposphere, and O₃ values varied over similar ranges – about 40 ppbv
529 in the NH and about 30 ppbv in the SH – during the two seasons (Fig. 12 in red and blue).

530 **O₃ enhancements.** The linear increase of O₃ with CO >100 ppbv highlights the
531 contribution of natural and anthropogenic pollution plumes lofted from continental areas into the
532 remote troposphere. In the NH, these events occur almost year-round (Figs. 13b–c and 13g–h).
533 Higher CO enhancements in the Pacific (Figs. 13g–h) than in the Atlantic (Figs. 13b–c) have
534 been observed before and attributed to sampling bias (Clark et al., 2015). Here, our findings
535 suggest a year-round influence of continental emissions on the Pacific atmosphere despite its
536 remoteness. Modeled back trajectories show that most air masses sampled in the NH during
537 ATom were influenced by long-range transport of continental emissions from Asia, Africa, and
538 North America (Fig. S6). Previous studies have shown anthropogenic and BB emission outflow
539 from Asia significantly contributed to O₃ pollution events measured over the northern Pacific or
540 in California (e.g., Heald et al., 2003; Jaffe et al., 2004; Lin et al., 2017). Intercontinental
541 transport of anthropogenic emissions from Europe can also contribute to the Asian outflow of
542 anthropogenic pollution (e.g., Bey et al., 2001; Liu et al., 2002; Newell and Evans, 2000).
543 Finally, O₃ enhancements in the northern Atlantic were frequently observed and attributed to
544 midlatitude anthropogenic and boreal forest fire emissions (e.g., Honrath et al., 2004; Martín et
545 al., 2006; Trickl et al., 2003). In the SH, polluted air is encountered more often in spring and
546 summer over the Atlantic, but springtime CO is greater than in other seasons over the Pacific
547 (Figs. 13d–e and 13i–j). During spring, median O₃ above 50 ppbv was measured throughout the
548 free troposphere in the southern midlatitudes (Fig. 12). Several air masses intercepted during
549 these flights originated from regions that were intensively burning at the time, notably equatorial
550 and southern Africa, Australia, and southern South America, contributing to the observed
551 enhanced O₃ and CO (Fig. S4). Our results expand on previous observation-based, but more
552 spatially and temporally limited, studies that highlighted collocated enhancements of O₃ and CO
553 at remote locations to show in situ evidence of frequent, large-scale influence of continental
554 outflow on O₃ in the remote troposphere in both oceans, and at almost all latitudes.

555

556 **5. Conclusion**

557 We present tropospheric O₃ distributions measured over remote regions of the Pacific and
558 Atlantic Oceans during two airborne chemical sampling projects: the four deployments of ATom
559 (2016–2018) and the five deployments of HIPPO (2009–2011). The data highlight several
560 regional- and large-scale features of O₃ distributions, and provide insight into current O₃
561 distributions in remote regions. The main findings are as follows:

- 562 - ATom and HIPPO provide a unique perspective on vertically-resolved global baseline O₃
563 distributions over the Pacific and Atlantic basins, and expand upon spatially-limited O₃
564 climatologies from long-term datasets to highlight large-scale features necessary for
565 model output and satellite retrieval validation.
- 566 - ATom and HIPPO O₃ data are consistent – where they overlap – with measurement-
567 based climatologies of tropospheric O₃ from well-established ozonesonde and
568 commercial aircraft monitoring programs. ATom and HIPPO seasonal median O₃
569 correlated well with corresponding seasonal median O₃ from ozonesondes ($R^2 > 0.7$),
570 giving confidence in the accurate depiction of the emerging global O₃ climatology by
571 these diverse research activities. ATom and HIPPO captured 30–71 % of O₃ variability
572 measured by ozonesondes launched in the vicinity of the aircraft flight tracks, and had the
573 same mode of the O₃ distribution as determined by IAGOS in the northern Atlantic
574 UTLS. This representativeness evaluation on global scales highlights the usefulness of
575 airborne observations to fill in the gaps of established but limited O₃ climatologies.
576 Higher O₃ loading in the NH compared to the SH is consistent with the heterogeneous
577 distribution of O₃ precursor emissions around the globe, mostly concentrated in the NH, a
578 result consistent with previous modeling studies and satellite observations. ATom
579 Atlantic vs. Pacific comparison reveals a similar O₃ distribution in the free troposphere
580 up to ~8 km in the middle- and high-latitudes, but not in the tropics. Similar O₃
581 distributions across latitude bands have been suggested in the past, but these studies were
582 limited to the northern midlatitudes. Conversely, other satellite, modeling, and
583 observation-based studies indicated significant O₃ longitudinal gradients. Here, our
584 findings are consistent with zonal transport smoothing the baseline O₃ distribution
585 longitudinally from the Pacific to the Atlantic. In the tropics, median O₃ mixing ratios are
586 about twice as high in the Atlantic than in the Pacific, due to a well-documented mixture
587 of dynamical patterns interacting with the transport of continental air masses.

- 588 - A comparison of seasonal O₃ vertical profiles did not reveal a marked seasonality in the
589 tropics, but instead highlighted the influence of specific events, most notably BB
590 emissions from Africa and South America, which have been extensively documented in
591 the literature. In the extra-tropics, the summer season was characterized by a steeper
592 tropospheric O₃ gradient driven by very low O₃ abundance in the MBL. Fall and winter
593 seasons generally led to near-constant O₃ mixing ratios from the surface to the upper
594 troposphere, while the highest O₃ abundance was recorded during the spring season when
595 more frequent and intense stratospheric intrusions and transport of air masses from
596 continental regions occur. ATom and HIPPO provide the first airborne in situ vertically-
597 resolved O₃ climatology covering both the Atlantic and Pacific Oceans in the NH and in
598 the SH. They confirm and extend the current understanding of O₃ variability in the
599 remote troposphere, built over several decades by airborne campaigns, monitoring
600 networks, and satellite observations.
- 601 - Overall, this paper highlights the value of the ATom and HIPPO datasets, which cover
602 spatial scales commensurate with the grid resolution of current Earth system models, and
603 further, are useful as a priori estimates for improved retrievals of tropospheric O₃ from
604 satellite remote sensing platforms. In addition, ATom and HIPPO in situ measurements
605 help to establish the quantitative legacy of global pollution transport and chemistry
606 through the evaluation of key, covarying species – in this case O₃ and CO, and reveal the
607 year-round pervasive influence of continental outflow on O₃ enhancements in the remote
608 troposphere. ATom and HIPPO datasets should be critical for improving the scientific
609 community's understanding of O₃ production and loss processes, and the influence of
610 anthropogenic emissions on baseline O₃ in remote regions. They provide a timely
611 addition to the Tropospheric Ozone Assessment Report (TOAR) effort to characterize the
612 global-scale O₃ distribution, and address some of the measurement gaps identified
613 therein.

614

615 **Author Contribution**

616 SCW and TBR designed the research (ATom and HIPPO). The measurements were done by IB,
617 JP, CRT, TC, RC, BD, GWD, JWE, RSG, EJH, KM, FLM, CS, and TBR. BJJ, RK, RQ, RS,
618 DWT, AMT, and JCW provided the ozonesonde measurements. HC, AG, and VT provided the

619 IAGOS measurements. Back trajectory calculations were provided by ER and KCA. IB, JP,
620 CRT, KCA, RC, AG, EJH, KM, DDP, RQ, ER, DWT, AMT, VT, JCW, SCW, and TBR
621 contributed to the discussion and interpretation of the results. IB, JP, and TBR wrote the paper.

622

623 **Competing interests**

624 The authors declare no competing interest.

625

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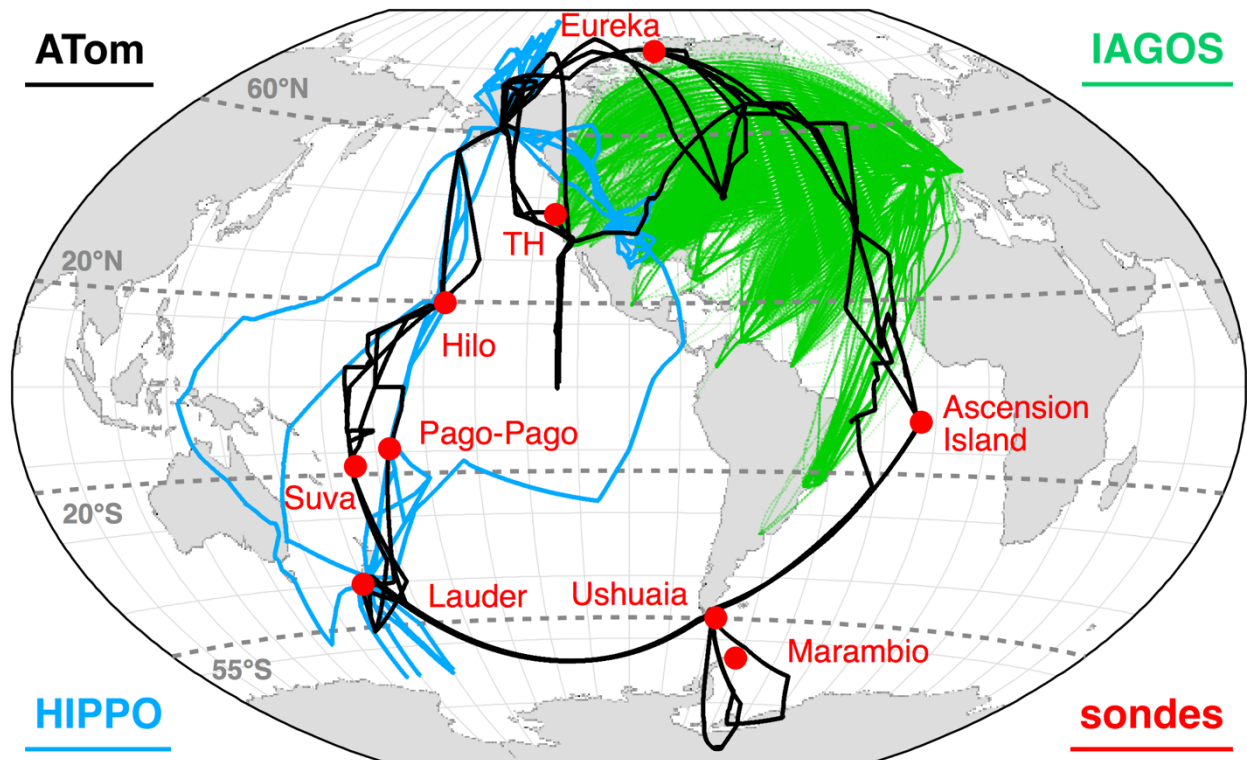


Figure 1 The location and flight tracks of all O₃ monitoring platforms used in this work are illustrated with different markers and colors. The ATom flight track is in black, the HIPPO flight track is in blue, IAGOS flight paths are in green, and the ozonesonde launching sites are indicated by the red markers. The dotted grey lines define the latitudinal bands over which individual ATom and HIPPO profiles were averaged to derive a regional O₃ distribution: the tropics (20° S – 20° N), the midlatitudes (55° S – 20° S; 20° N – 60° N), and the high-latitudes (90° S – 55° S; 60° N – 90° N). Only data from remote oceanic flight segments of ATom and HIPPO missions were used in this work.

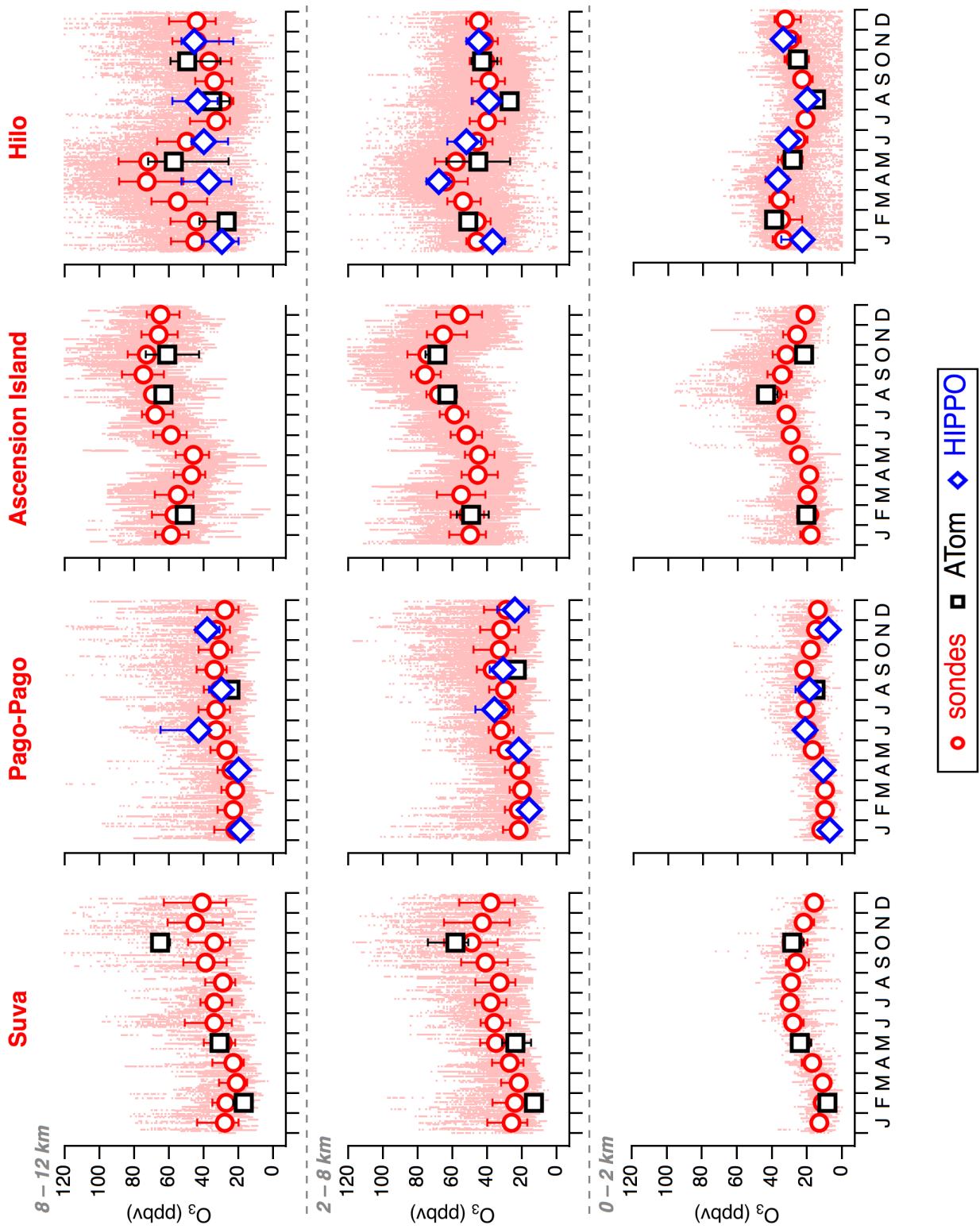


Figure 2 Comparison of ATom (black squares) and HIPPO (blue diamonds) monthly median O₃ with ozonesonde (red circles) records from the four tropical sites. Markers indicate the median and the bars indicate the 25th and 75th percentiles. The three rows, from bottom to top, correspond to the boundary layer (0–2 km), the free troposphere (2–8 km), and the UTLS (8–12 km). The pink dots show every O₃ data point measured by ozonesondes for the timeframes indicated in Table S2.

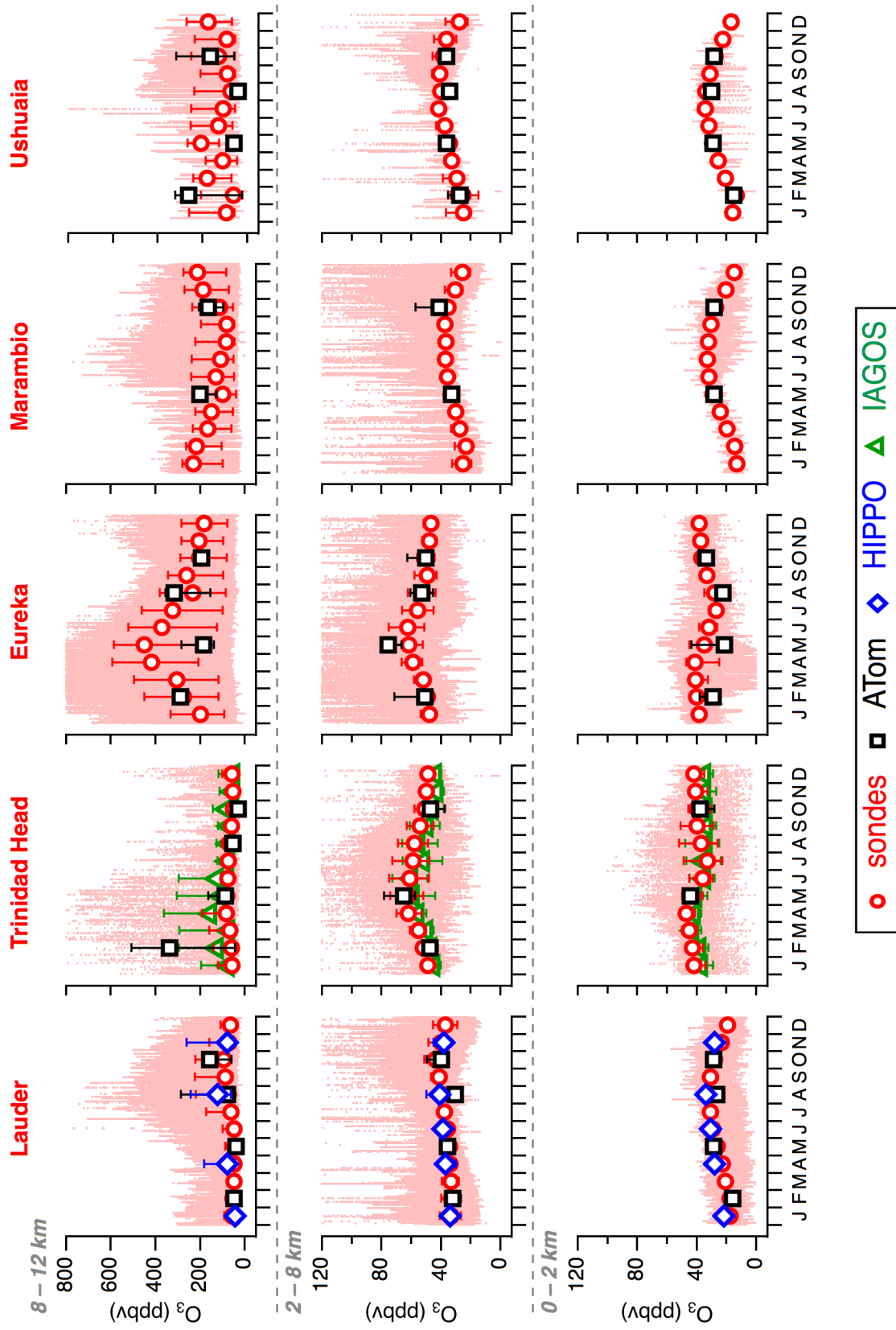


Figure 3 Same as in Figure 2 but for ozonesonde launching sites located in the middle- and high-latitudes. O₃ data obtained from the IAGOS program (green triangles) during descents into San Francisco Bay-area airports were also added to the Trinidad Head site for comparison.

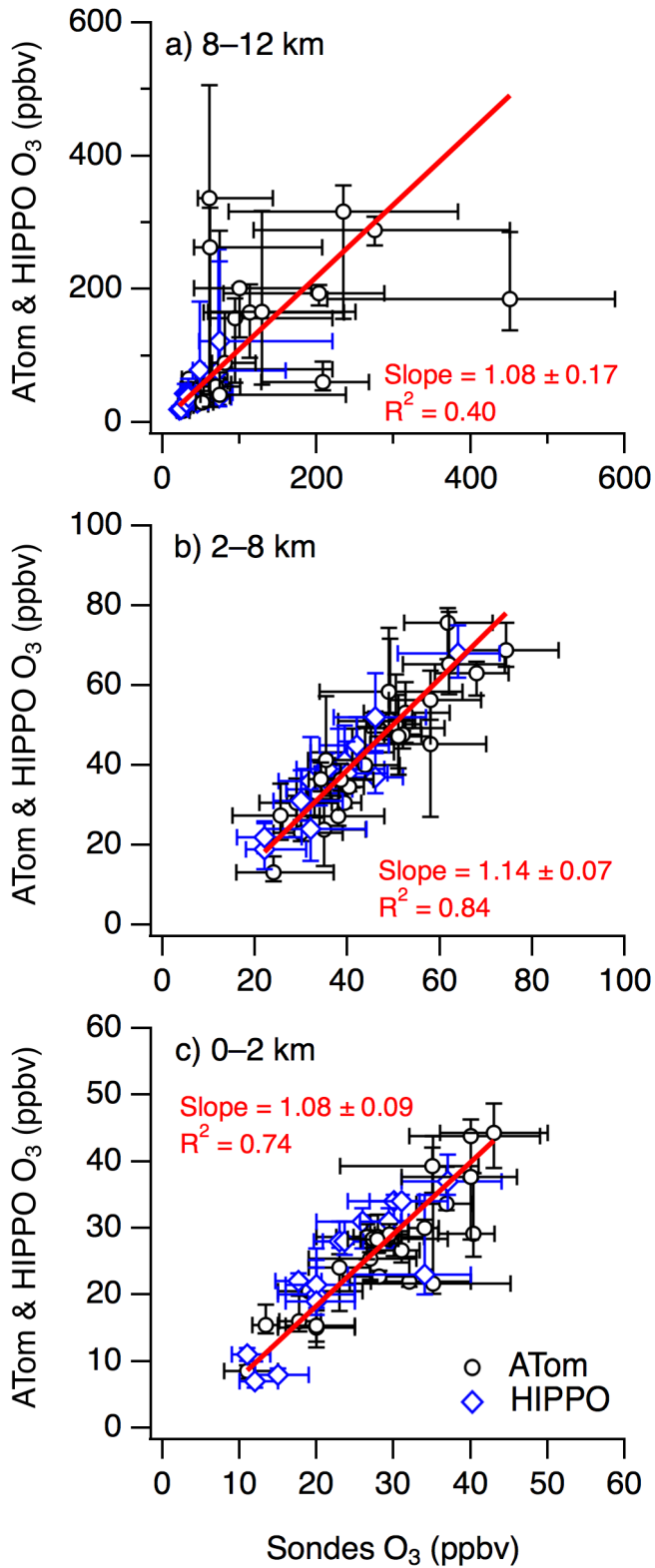


Figure 4 ATom (black circles) and HIPPO (blue diamonds) combined monthly median O₃ vs. monthly median O₃ from ozonesondes at the nine sites considered in this study. The three panels

indicate the correlations for a) the UTLS (8–12 km), b) the free troposphere (2–8 km), and c) the boundary layer (0–2 km). The orthogonal regression fits are two-sided but not weighted.

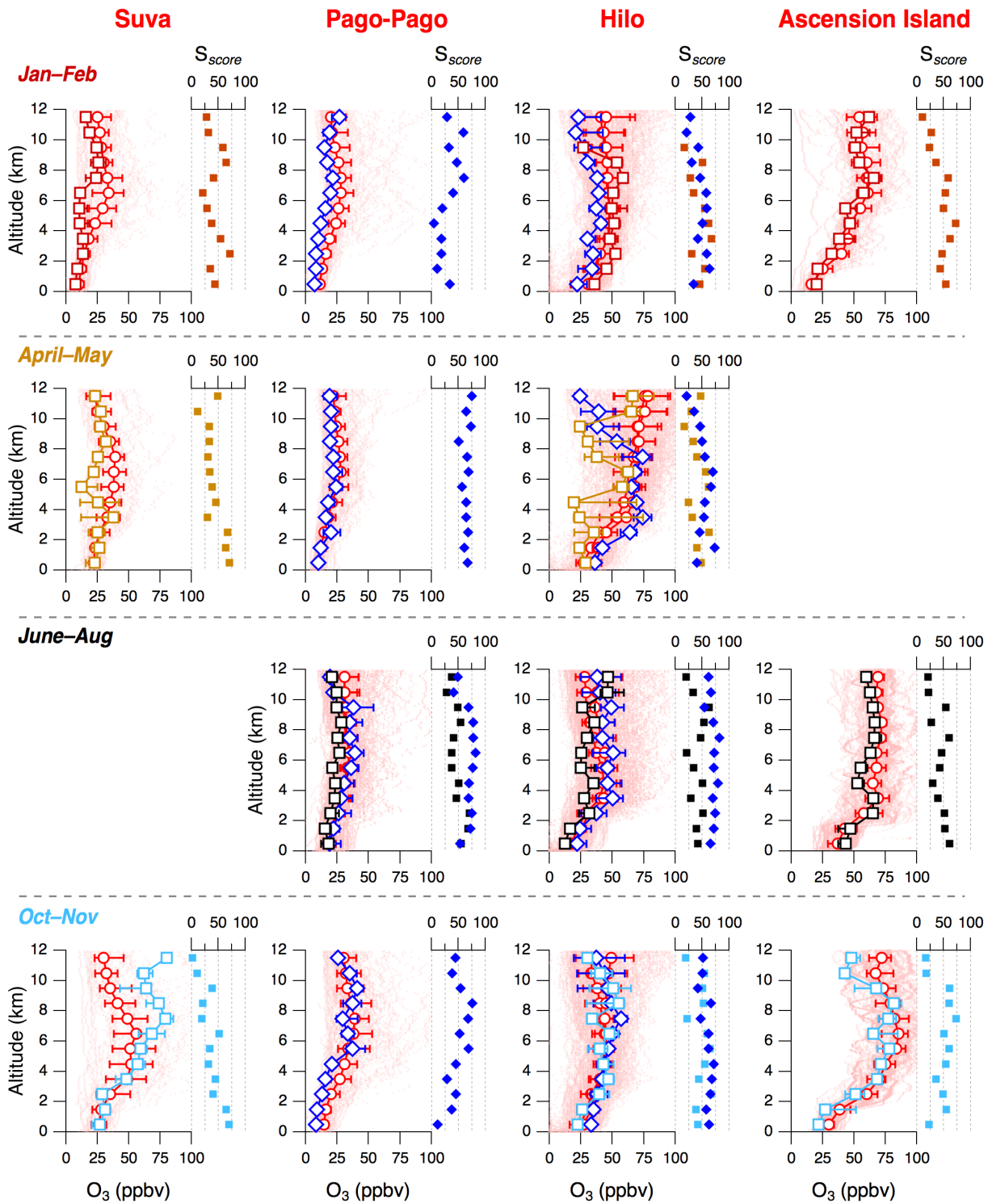


Figure 5 Seasonal comparison of 1 km-vertically-binned ATom (colored squares) and HIPPO (blue diamonds) median O_3 with ozonesonde (red circles) records at four sites in the tropics (Suva in Fiji, Pago-Pago in American Samoa, Hilo in Hawaii, and Ascension Island). Markers indicate the median and the bars are the 25th and 75th percentiles. The S_{score} is a metric of how well ATom

and HIPPO 1 km-binned O₃ probability distribution functions (PDFs) overlap with the corresponding 1 km-binned O₃ PDFs from ozonesondes. The S_{score} shown with squares compares ATom with ozonesondes, and the S_{score} shown with blue diamonds compares HIPPO with ozonesondes. The pink dots show every O₃ data point measured by ozonesondes for the timeframes indicated in Table S2.

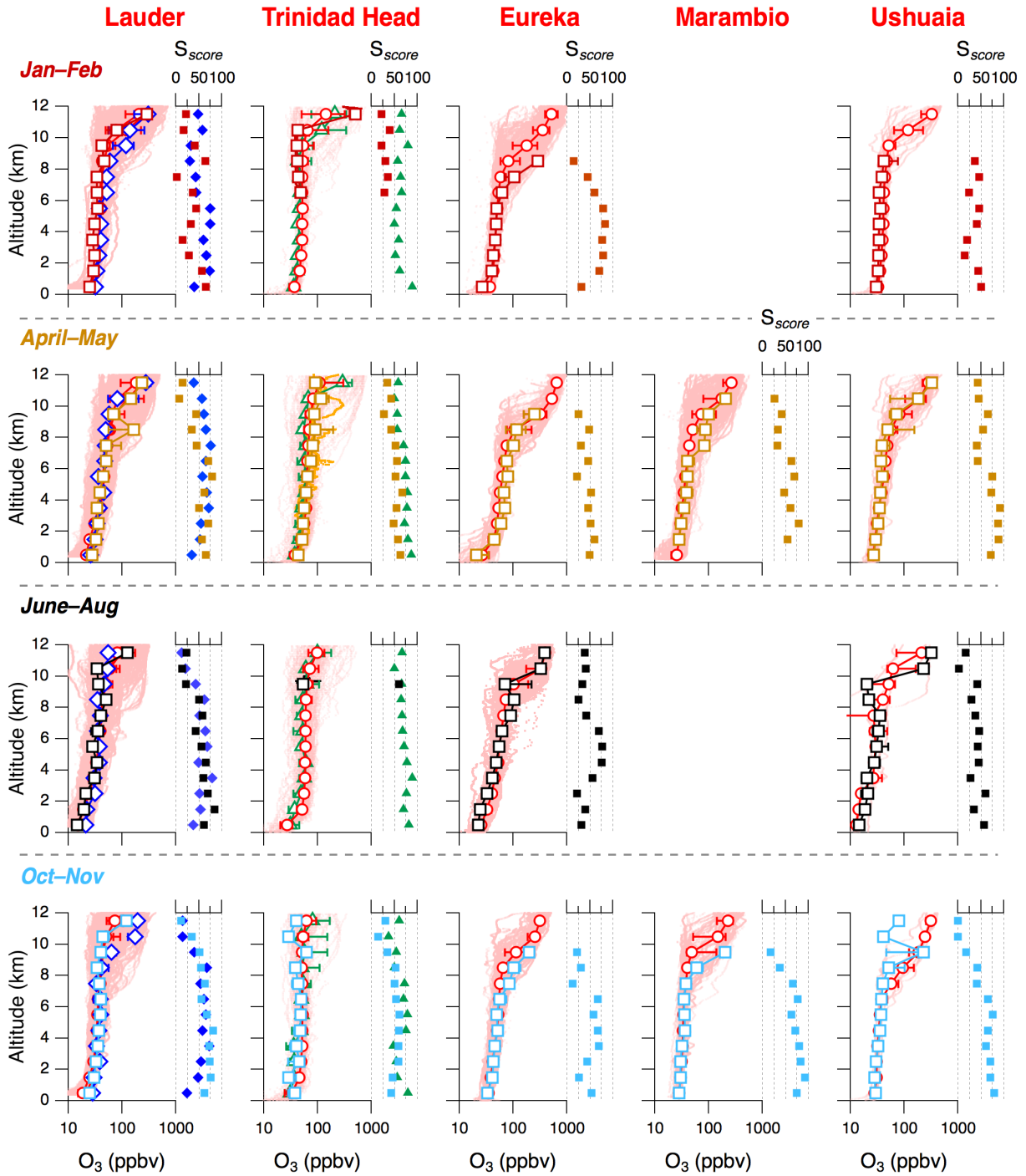


Figure 6 Same as in Figure 5 but for ozonesonde launching sites located in middle- and high-latitudes (Lauder in New Zealand, Trinidad Head in the USA, Eureka in Canada, Ushuaia in Argentina, and Marambio in Antarctica). O₃ data obtained from the IAGOS program (green triangles) during descents into San Francisco Bay-area nearby airports were also added to the Trinidad Head site for comparison.

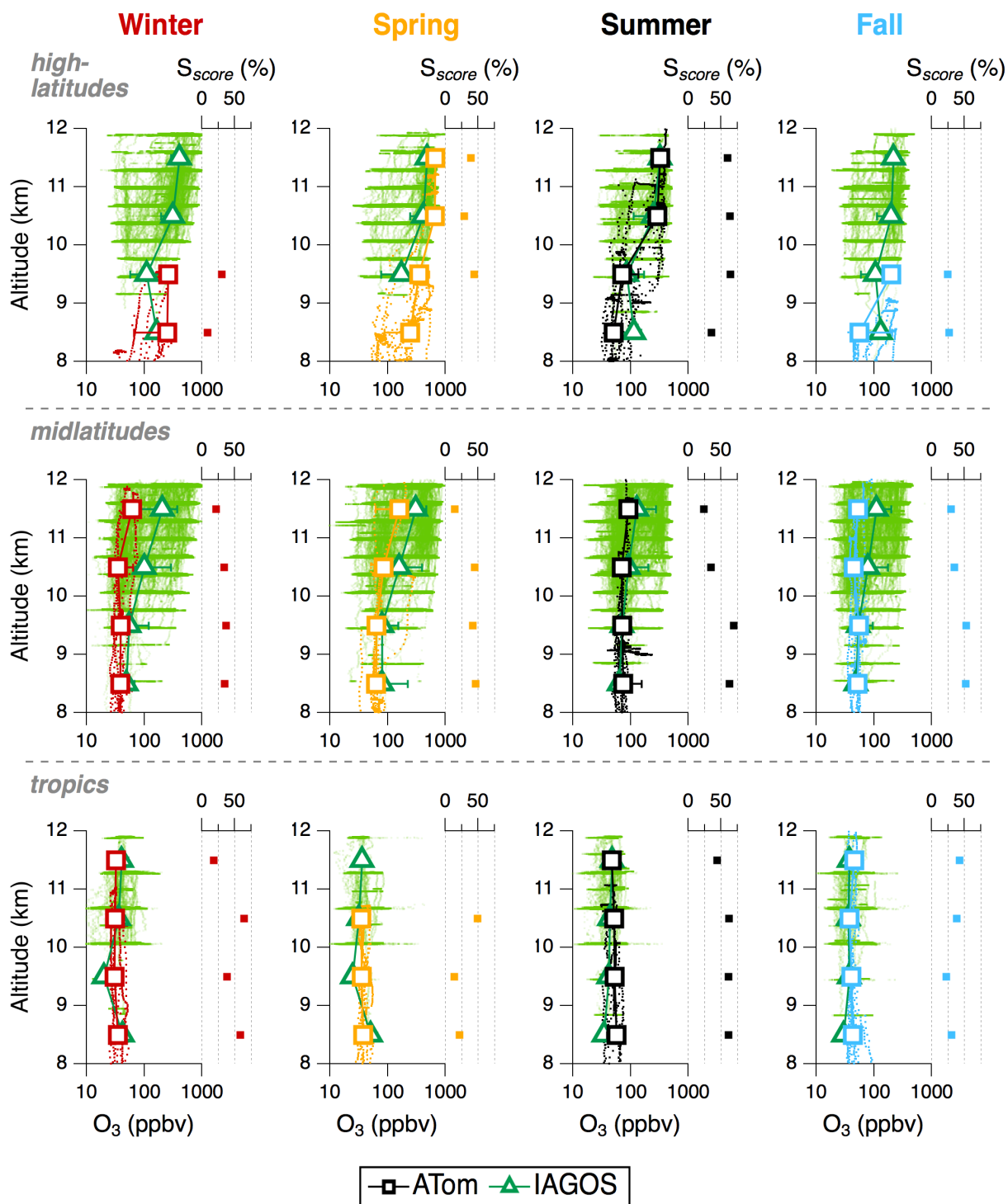


Figure 7 Seasonal comparison of 1 km-binned ATOm (colored squares) median O_3 with IAGOS (green triangles) in the northern Atlantic UTLS. Markers indicate the median and the bars are the 25th and 75th percentiles. The three different rows indicate the latitudinal bands. The four columns

indicate the seasons. The green dots show every O₃ data point measured by IAGOS flights for the timeframe indicated in Table S1.

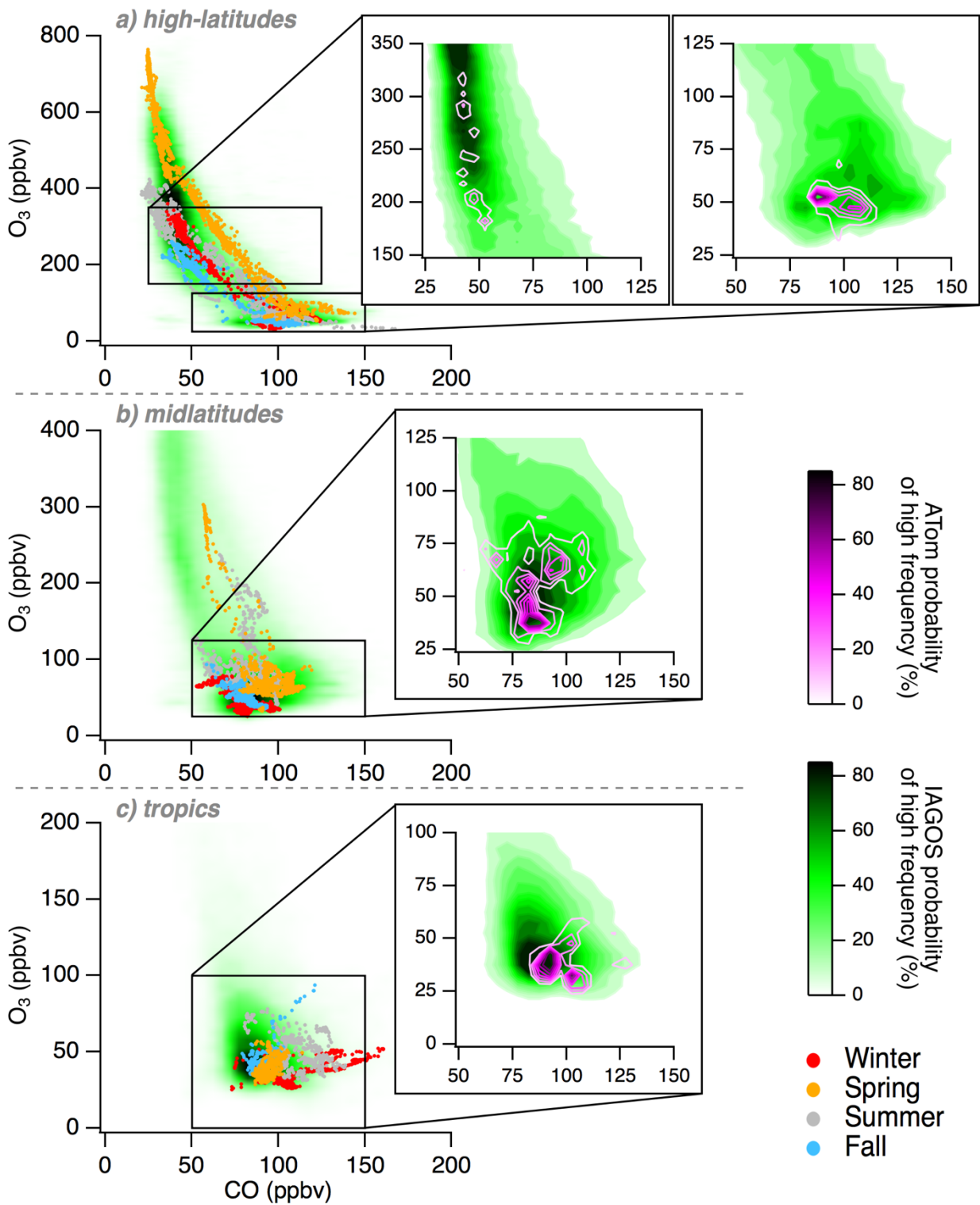


Figure 8 IAGOS and ATom seasonal O₃ vs. CO scatterplots, with insets showing the most frequent O₃ values measured during IAGOS and ATom. ATom seasonal deployments are

colored according to the legend. The frequency gradient of O₃ counts is illustrated by the color scales (green for IAGOS, magenta for ATom). ATom measurements have been combined for the frequency gradients shown in the insets. The probability of high frequency refers to the probability of finding frequently measured O₃ values within the contour boundaries

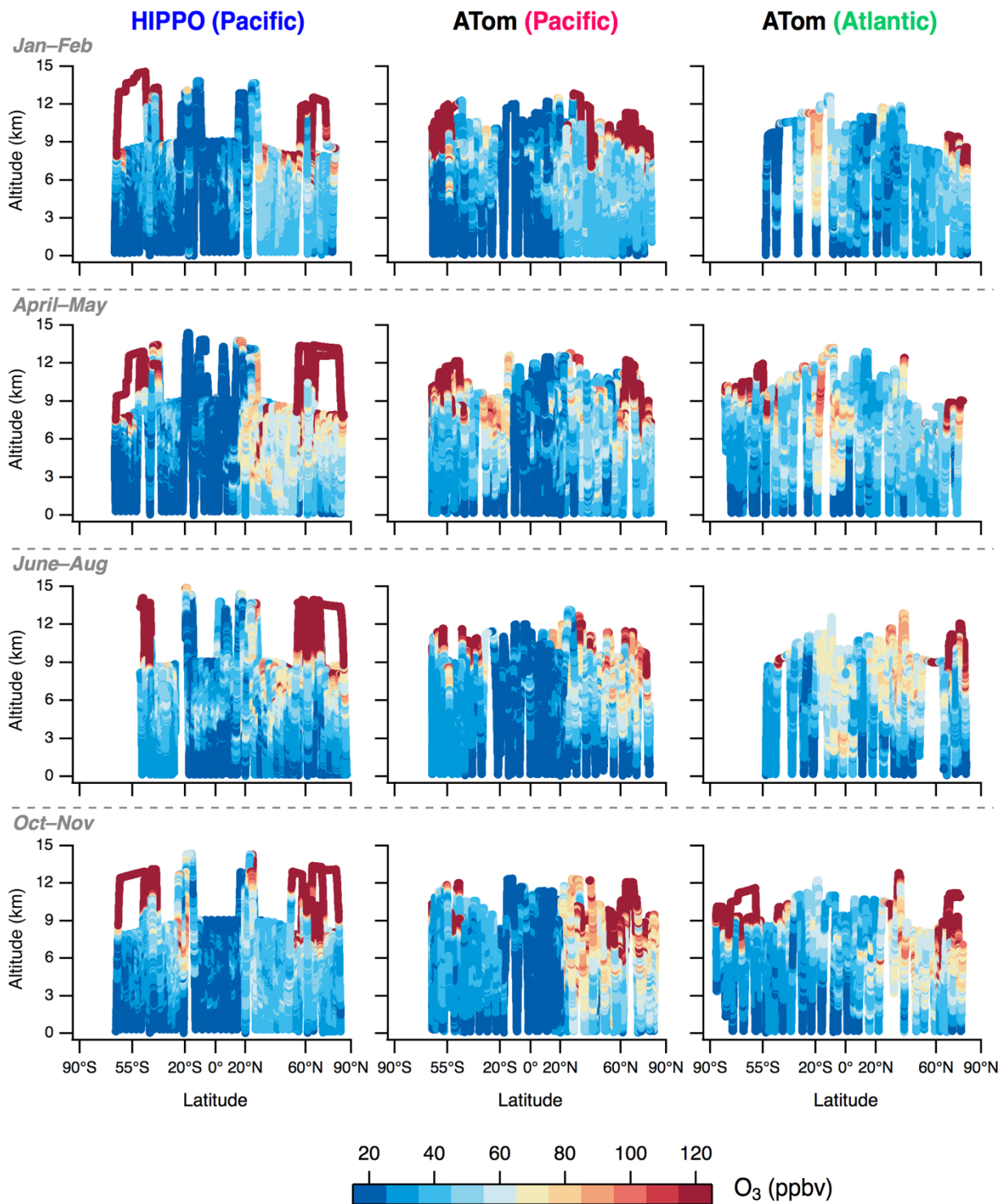


Figure 9 Global-scale distribution of tropospheric O₃ for each ATom and HIPPO seasonal deployment. The rows separate the seasonal deployments, while the columns indicate the mission and the ocean basin. The O₃ color-scale ranges from 20 to 120 ppbv, and all values outside of this

range are shown with the same extremum color (red for values > 120 ppbv, blue for values < 20 ppbv). HIPPO deployments in June and August were combined together.

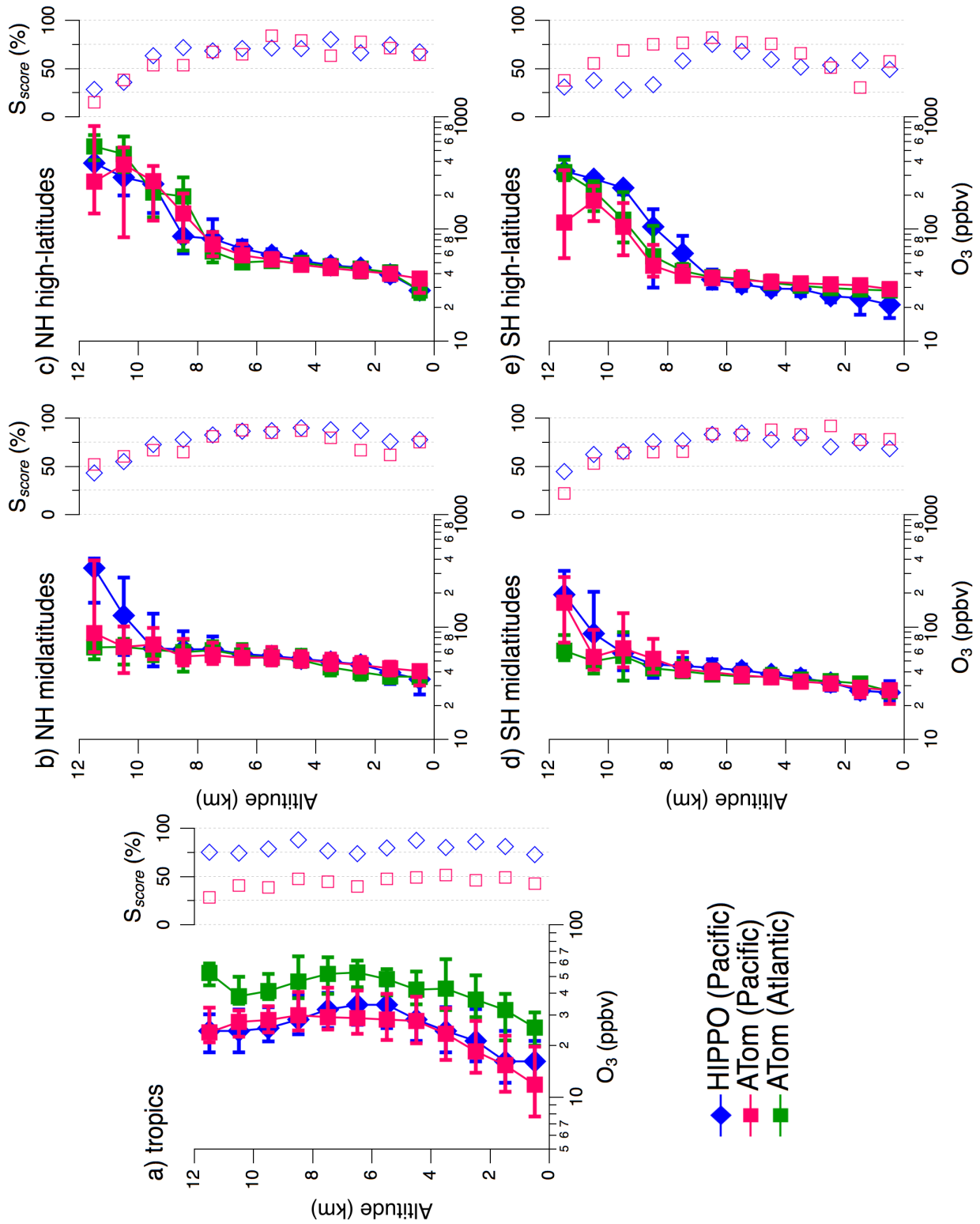


Figure 10 Vertically-resolved O₃ distributions from 0–12 km are plotted for the Atlantic (ATom in green) and for the Pacific (ATom in pink, HIPPO in blue). The five broad latitude regions correspond to the data parsing illustrated by Fig. 1. Markers indicate median O₃, and bars are the

25th and 75th percentiles, per 1 km altitude bin. Note the log scale on the x-axis. S_{score} values resulting from the comparison of HIPPO and ATom Pacific distributions are shown with blue diamonds, and from the comparison of ATom Atlantic and Pacific distributions with pink squares.

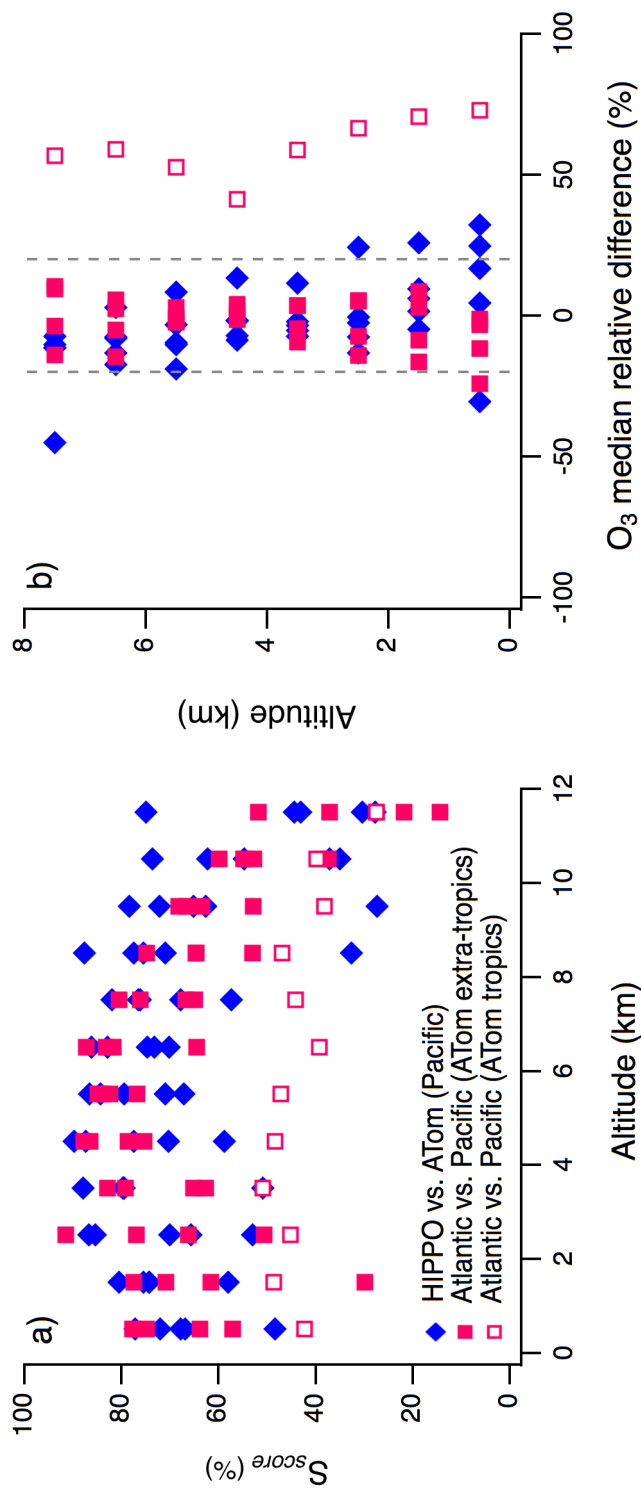


Figure 11 All S_{score} values from Fig. 10 are shown in panel a) and plotted against altitude. The HIPPO and ATom comparison in the Pacific basin is shown with blue diamonds, and a comparison of the Atlantic and Pacific basins during ATom is shown with filled pink squares for the extra-

tropics and open pink squares for the tropics. The relative difference of median O₃ from 0 to 8 km given in Fig. 10 is shown in panel b), with the same color and marker code as in panel a). The dotted grey lines indicate a relative difference of 20 %.

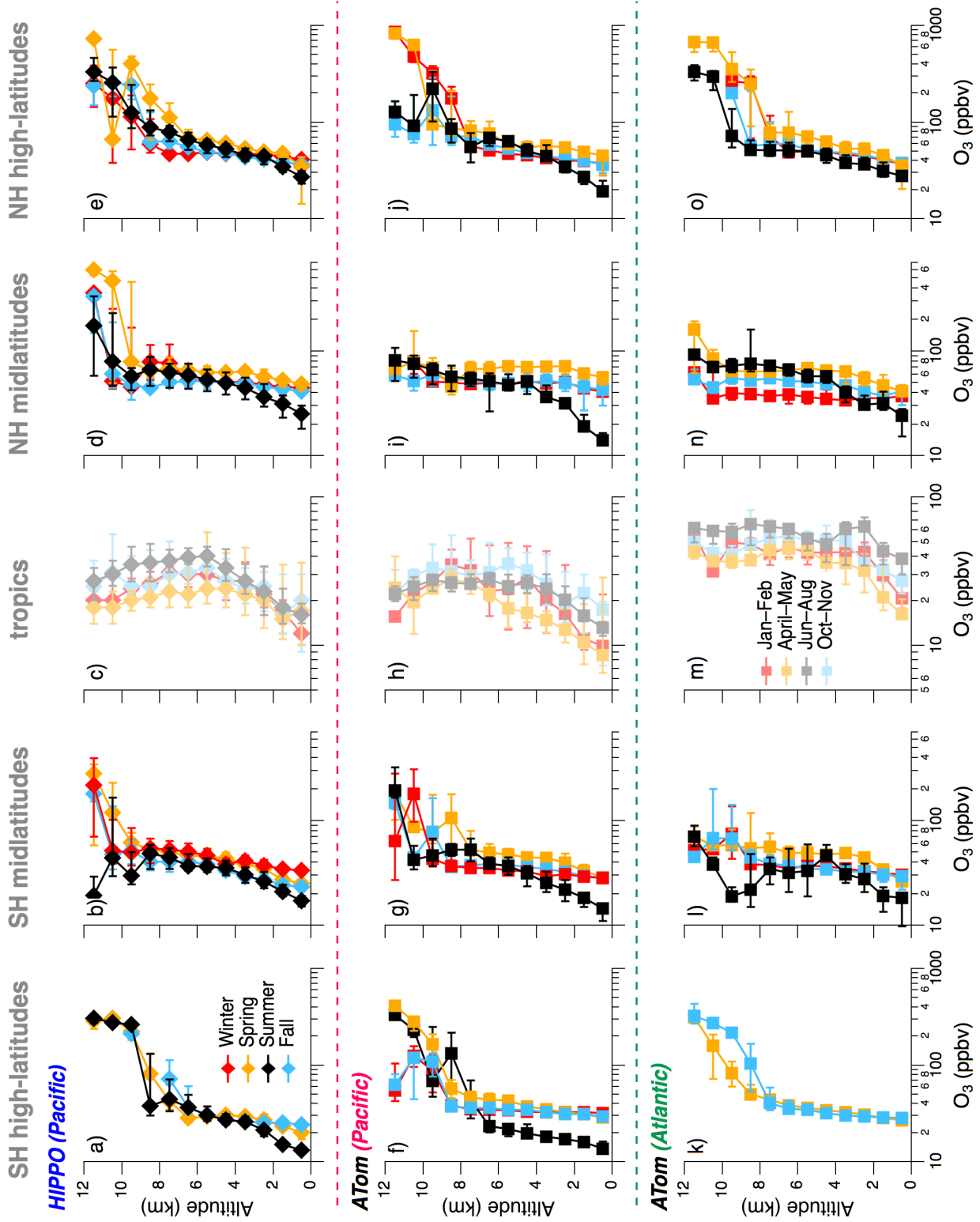


Figure 12 Seasonal variability of regional O₃ distribution in the Pacific (HIPPO in the first and ATom in the second row) and in the Atlantic (ATom in the third row). The colors designate the

local seasons with red as winter, gold as spring, black as summer, and blue as fall (corresponding months are indicated for the tropics, with lighter colors). The markers and associated bars correspond to the median, 25th and 75th percentiles, respectively, of O₃ distribution in every 1 km altitude bin. Note the logarithmic scale on the x-axes in all panels, and the changing scale with latitudinal bin.

Figure 13 O₃ vs. CO plots using combined ATom and HIPPO data. Each panel denotes a different latitudinal band in each basin. Seasonal deployments are colored according to the legend. Note the logarithmic scale on the y-axis in all panels, and the changing scale with latitudinal bin

