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## 1 Arctic tropospheric ozone: assessment of current knowledge 2 and model performance

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31 **Abstract.** As the third most important greenhouse gas (GHG) after CO<sub>2</sub> and methane, tropospheric ozone (O<sub>3</sub>) is  
32 also an air pollutant causing damage to human health and ecosystems. This study brings together recent research  
33 on observations and modeling of tropospheric O<sub>3</sub> in the Arctic, a rapidly warming and sensitive environment. At  
34 different locations in the Arctic, the observed surface O<sub>3</sub> seasonal cycles are quite different. Coastal Arctic  
35 locations, for example, have a minimum in the springtime due to O<sub>3</sub> depletion events resulting from surface  
36 bromine chemistry. In contrast, other Arctic locations have a maximum in the spring. The 12 state-of-the-art  
37 models used in this study lack the surface halogen chemistry needed to simulate coastal Arctic surface O<sub>3</sub> depletion  
38 in the springtime, however, the multi-model median (MMM) has accurate seasonal cycles at non-coastal Arctic  
39 locations. There is a large amount of variability among models, which has been reported previously, and we show  
40 that there continues to be no convergence among models, nor improved accuracy in simulating tropospheric O<sub>3</sub>  
41 and its precursor species. The MMM underestimates Arctic surface O<sub>3</sub> by 5% to 15% depending on the location.  
42 The vertical distribution of tropospheric O<sub>3</sub> is studied from recent ozonesonde measurements and the models. The  
43 models are highly variable, simulating free-tropospheric O<sub>3</sub> within a range of +/- 50% depending on the model  
44 and the altitude. The MMM performs best, within +/- 8% at most locations and seasons. However, nearly all  
45 models overestimate O<sub>3</sub> near the tropopause (~300 hPa or ~8 km), likely due to ongoing issues with  
46 underestimating the altitude of the tropopause and excessive downward transport of stratospheric O<sub>3</sub> at high  
47 latitudes. For example, the MMM is biased high by about 20% at Eureka. Observed and simulated O<sub>3</sub> precursors



48 (CO, NO<sub>x</sub> and reservoir PAN) are evaluated throughout the troposphere. Models underestimate wintertime CO  
49 everywhere, likely due to a combination of underestimating CO emissions and possibly overestimating OH.  
50 Throughout the vertical profile (compared to aircraft measurements), the MMM underestimates both CO and NO<sub>x</sub>  
51 but overestimates PAN. Perhaps as a result of competing deficiencies, the MMM O<sub>3</sub> matches the observed O<sub>3</sub>  
52 reasonably well. Our findings suggest that despite model updates over the last decade, model results are as highly  
53 variable as ever, and have not increased in accuracy for representing Arctic tropospheric.

## 54 **1 Introduction**

55 Tropospheric ozone (O<sub>3</sub>) is the third most important greenhouse gas (GHG) after CO<sub>2</sub> and methane (IPCC, 2021),  
56 and is an air pollutant causing damage to human health (WHO, 2013). It also causes damage to vegetation  
57 following dry deposition to the surface (U.S. EPA, 2013). However, our knowledge about the sources and sinks  
58 of tropospheric O<sub>3</sub> is still uncertain (AMAP, 2015; 2022; Gaudel et al., 2018), in particular in regions where fewer  
59 observations exist, and where our understanding of key processes is still evolving. The Arctic is one such region  
60 where few long-term measurements of O<sub>3</sub> exist and measurements of compounds that are important for producing  
61 and destroying O<sub>3</sub> in the atmosphere are scarce at the surface and even more so in the free troposphere. Progress  
62 has been made recently in terms of our understanding of certain processes and a picture is emerging about the  
63 distribution of Arctic tropospheric O<sub>3</sub> as well as seasonal cycles and trends at different locations (e.g., Young et  
64 al, 2018; Tarasick et al, 2019b). In particular, the connection between surface O<sub>3</sub> depletion episodes and halogens  
65 is now well established (e.g., Simpson et al., 2007; Abbatt et al., 2012).

66 However, the role of natural cycles in the Arctic O<sub>3</sub> budget relative to O<sub>3</sub> produced from anthropogenic emissions  
67 and how that relationship is changing in response to rapid warming in the Arctic are still uncertain. Arctic warming  
68 and associated development in the Arctic are also driving changes in local anthropogenic emissions which could  
69 already be leading to changes in the relative contributions of O<sub>3</sub> produced due to long-range transport of mid-  
70 latitude anthropogenic emissions and O<sub>3</sub> produced from within or near-Arctic anthropogenic emissions. Increases  
71 in emissions, such as from shipping (Gong et al., 2018) or boreal fires can affect Arctic air quality (Schmale et al.,  
72 2018).

73 Ozone radiative forcing resulting from changes in tropospheric O<sub>3</sub> in the Arctic is highly sensitive to altitude. The  
74 sensitivity of the Arctic O<sub>3</sub> vertical profile, and resultant forcing, from particular anthropogenic emission sources  
75 and regions, vary substantially with altitude (Rap et al., 2015). Arctic surface O<sub>3</sub> may be most sensitive to European  
76 or local sources (Sand et al., 2015; AMAP 2015; 2022), whereas emissions from North American and Asian  
77 sources are more important in the mid- and upper troposphere (Monks et al., 2015; Wespes et al., 2012). Therefore,  
78 a combination of varied source sensitivities in the vertical profile and the increased efficacy of longwave O<sub>3</sub> forcing  
79 with altitude in the troposphere leads to a complex picture in terms of drivers of climate forcing by Arctic O<sub>3</sub>. The  
80 presence of temperature inversions in the Arctic lower troposphere may result in negative local forcing (Rap et al.,  
81 2015; Flanner et al., 2018), in particular for local sources such as shipping (Marelle et al., 2018). Hence, to improve  
82 the quantification of O<sub>3</sub> radiative effects in the Arctic there is a need first to assess model performance in terms of  
83 seasonal cycles and vertical distributions. The annual mean vertical distributions of O<sub>3</sub> and CO were examined in  
84 AMAP (2022) and Whaley et al. (2022) as compared to TES and MOPITT satellite retrievals. Those studies



85 showed good agreement between models and satellite measurements for O<sub>3</sub> in the free troposphere, where it is a  
86 strong GHG.

87 This paper assesses the current state of knowledge about the dynamics of Arctic tropospheric O<sub>3</sub> and the ability of  
88 a suite of current chemistry-transport and chemistry-climate models to simulate seasonal cycles of O<sub>3</sub> and selected  
89 precursors. We first review our current understanding of sources and sinks of Arctic tropospheric O<sub>3</sub> in Section 2.  
90 We summarize the models used in this study in Section 3 and the recent findings from satellite observations in  
91 Section 4. We then examine the extent to which our understanding of Arctic tropospheric O<sub>3</sub> can explain observed  
92 seasonal cycles at different surface sites in the Arctic and assess the ability of models to simulate observed  
93 distributions (Section 5). We also examine vertical distributions of O<sub>3</sub> and its precursors and the extent to which  
94 models are able to capture observed seasonal variations (Section 6). Finally, conclusions are presented in Section  
95 7. Trends in Arctic tropospheric O<sub>3</sub> over the last 20-30 years and possible changes in seasonal cycles are presented  
96 in a companion paper and compared to results from a subset of these models (Law et al., 2022).

## 97 **2. Arctic O<sub>3</sub>: sources and sinks**

98 This section reviews tropospheric O<sub>3</sub> sources and sinks that are particularly relevant to the Arctic region, and many  
99 of these processes are shown in the schematic in Figure 1.

### 100 **2.1 Ozone sources**

101 Tropospheric O<sub>3</sub> is a secondary air pollutant, which is not directly emitted but produced from the photochemical  
102 reactions of anthropogenic and natural precursor emissions of VOCs, CO and CH<sub>4</sub> in the presence of NO<sub>x</sub>. Besides  
103 significant anthropogenic sources of these O<sub>3</sub> precursors, there are also important natural sources for these species,  
104 such as boreal fires, lightning, vegetation and transport of O<sub>3</sub> from the stratosphere, which show marked seasonal  
105 and inter-annual variations (Figure 1). Away from the surface, and in remote environments the tropospheric O<sub>3</sub>  
106 lifetime is around 20 days or more (Young et al., 2013), which facilitates the long-range transport of O<sub>3</sub> in the  
107 troposphere. Production of O<sub>3</sub> from lower latitude emission sources and its subsequent transport to the Arctic is a  
108 substantial source of Arctic tropospheric O<sub>3</sub>, where the dry Arctic conditions and stably stratified atmosphere  
109 further prolong the O<sub>3</sub> lifetime. In addition, the stratosphere-troposphere exchange of O<sub>3</sub> makes a substantial  
110 contribution to the Arctic O<sub>3</sub> budget, where a lower tropopause height compared to the tropics facilitates the import  
111 of stratospheric air masses rich in O<sub>3</sub>. The weak in-situ O<sub>3</sub> formation in the Arctic relative to lower latitudes  
112 increases the relative importance of this exchange. More recently, a new understanding has emerged regarding  
113 contributions to Arctic surface O<sub>3</sub> from both anthropogenic and natural near-Arctic sources of O<sub>3</sub> precursors.

114 Downward transport of O<sub>3</sub> from the stratosphere is an important source of O<sub>3</sub> in the Arctic troposphere and may  
115 be key in driving seasonality in Arctic tropospheric O<sub>3</sub> (Shapiro et al., 1987, Hess and Zbinden, 2013, Ancellet et  
116 al., 2016). The Liang et al. (2009) modeling study suggests that in spring (March and April), most of the O<sub>3</sub> in the  
117 Arctic upper troposphere originates from the stratospheric injection (78%) and that 20-25% of surface O<sub>3</sub>  
118 originates from direct injection of O<sub>3</sub> or the injection of NO<sub>y</sub> and secondary O<sub>3</sub> formation. Analysis of observations  
119 by Tarasick et al. (2019a) is consistent with this picture. Global model simulations conducted as part of the Coupled  
120 Model Intercomparison Project Phase 6, suggest an increase in near-surface O<sub>3</sub> over the Arctic during the 21st



121 century, driven by increased stratospheric O<sub>3</sub> import into the troposphere, particularly in winter (Zanis et al., 2022).  
122 In contrast, during summer, the dominant source of Arctic tropospheric O<sub>3</sub> is in-situ production in the Arctic,  
123 which in July contributes more than 50% of O<sub>3</sub> in the Arctic boundary layer and 30-40% in the free troposphere  
124 (Walker et al., 2012). This study also showed that the transport of peroxyacetyl nitrate (PAN) from lower latitudes  
125 is the dominant source of NO<sub>x</sub>, driving in-situ O<sub>3</sub> production at the surface in late spring and early summer.  
126 Methane (CH<sub>4</sub>) is a key precursor for tropospheric O<sub>3</sub>, via its oxidation in the presence of sufficient NO<sub>x</sub>.  
127 Anthropogenic CH<sub>4</sub> emissions are estimated to be responsible for around half of the global radiative forcing due  
128 to tropospheric O<sub>3</sub> from pre-industrial to present-day (Stevenson et al. 2013). Fiore et al. (2008) estimated that  
129 anthropogenic CH<sub>4</sub> emissions contribute 15% to the annual average total global O<sub>3</sub> burden (including natural and  
130 anthropogenic sources). Based on parameterised source-receptor sensitivities for a range of CMIP6 SSP scenarios,  
131 Turnock et al. (2019) illustrated the significant contribution of CH<sub>4</sub> to future O<sub>3</sub> concentration reductions at high  
132 latitudes. Using a similar approach, based on parameterised responses to O<sub>3</sub> precursor emission perturbations found  
133 that CH<sub>4</sub> dominates the sensitivity of Arctic O<sub>3</sub> to anthropogenic emissions (AMAP, 2015). CH<sub>4</sub> accounts for  
134 approximately 40% of the Arctic O<sub>3</sub> response to precursor emission perturbations (AMAP, 2015).

135 Import of O<sub>3</sub> and its precursors from lower latitudes associated with episodes of long-range transport of  
136 anthropogenic or biomass burning pollution leads to enhancements in Arctic tropospheric O<sub>3</sub> (Wespes et al., 2012;  
137 Monks et al., 2015; Ancellet et al., 2016). Whilst very low levels of NO<sub>x</sub> within the Arctic, away from local  
138 sources, often limit local O<sub>3</sub> production, the release of NO<sub>x</sub> from thermal decomposition of peroxy-acetyl nitrate  
139 (PAN) (an important NO<sub>x</sub> reservoir) imported from lower latitudes, can lead to in-situ production of O<sub>3</sub>,  
140 particularly in the warmer Arctic summer lower troposphere (Wespes et al., 2012; Arnold et al., 2015).  
141 Investigation of long-range transport of O<sub>3</sub> precursors has shown efficient export of PAN from East Asia to the  
142 North Pacific, with relative contributions to long-range O<sub>3</sub> transport of 35% in spring and 25% in summer (Jiang  
143 et al., 2016). Ship observations over the Arctic and Bering Seas also identified events of long-range pollution  
144 transport with enhancements in O<sub>3</sub> (Kanaya et al., 2019).

145 Recently, there has been progress in improving knowledge of local O<sub>3</sub> precursor sources. Surface O<sub>3</sub> in summer is  
146 already influenced by shipping NO<sub>x</sub> emissions along the northern Norwegian coast (Marelle et al., 2016; Marelle  
147 et al., 2018) and the Northwest Passage (Aliabadi et al., 2015). Marelle et al., (2018) showed for a 2050 scenario,  
148 including diversion shipping in the Arctic, shipping would become the main surface O<sub>3</sub> source. Tuccella et al.  
149 (2017) showed that background O<sub>3</sub> is influenced by emissions downwind of oil and gas extraction platforms in the  
150 southern Norwegian Sea. Granier et al. (2006) predicted the increase in shipping activity during the summer would  
151 increase O<sub>3</sub> levels by a factor of 2-3 in the coming decades, with maximum increases (> 20 ppbv) occurring in the  
152 Canadian Archipelago, Beaufort Sea, central Arctic Ocean, and the Siberian sector of the Arctic.

153 Natural sources of Arctic tropospheric O<sub>3</sub> precursors include lightning NO<sub>x</sub>, emissions of NO<sub>x</sub> and reactive VOCs  
154 from the snowpack (Honrath et al., 1999; Guimbaud et al., 2002; Hornbrook et al., 2016; Pernov et al., 2021), and  
155 natural emissions of VOCs from high latitude vegetation (Holst et al., 2010; Ghirardo et al., 2020), and the Arctic  
156 Ocean (Mungall et al., 2017). Evidence from both observations and models suggests that boreal fires are also an  
157 important source of O<sub>3</sub> precursors and NO<sub>x</sub> reservoir species like PAN, in spring and summer, with impacts on  
158 Arctic O<sub>3</sub> (Thomas et al., 2013; Arnold et al., 2015; Viatte et al., 2015; Ancellet et al., 2016).



## 159 2.2 Ozone sinks

160 Photochemical loss of O<sub>3</sub> is mainly via photolysis in the presence of water vapor or direct reaction of O<sub>3</sub> with  
161 hydroperoxyl or hydroxyl radicals (HO<sub>2</sub> or OH). Photochemical destruction involving the hydroperoxyl radical  
162 (HO<sub>2</sub>) may be particularly important in the Arctic where water vapor abundances are low (Arnold et al. 2015).  
163 Where local emission sources give rise to high NO<sub>x</sub> concentrations in urban regions or regions of shipping activity,  
164 O<sub>3</sub> loss via titration with NO can be dominant (Thorp et al., 2021; Raut et al., 2022). Dry deposition of O<sub>3</sub> and its  
165 precursors to ice and ocean surfaces is slower than to vegetated terrestrial surfaces (Figure 1). Van Dam et al.  
166 (2016) reported O<sub>3</sub> dry deposition velocities that were 5 times higher over Arctic snow-free tundra in the summer  
167 months at Toolik Lake (northern Alaska) compared to the snow-covered ground. Dry deposition, combined with  
168 possible chemical loss (e.g. involving Biogenic-Volatile Organic Compounds, BVOCs) producing lower O<sub>3</sub>  
169 concentrations during stable (lower light) night conditions may explain the different diurnal cycle observed at this  
170 tundra site compared to Arctic coastal locations. Interestingly, gradient studies at Barrow showed a positive  
171 gradient with height during O<sub>3</sub> depletion events (ODE) and atmospheric mercury depletion events (AMDE)  
172 suggesting that O<sub>3</sub> was removed at the surface due to fast photochemical reactions at or close to snow surfaces  
173 initiated by the release of halogen species (Skov et al., 2006). During ODEs at Arctic sites in the Canadian  
174 archipelago (Alert, Resolute, and Eureka), vertical profiles show ozone is typically uniformly depleted in the  
175 boundary layer whereas a positive gradient is observed above the boundary layer (Tarasick and Bottenheim, et al.,  
176 2002).

177 During Arctic spring, photochemical cycling of halogens in so-called ‘bromine explosion’ events leads to rapid  
178 depletion of surface O<sub>3</sub> to low or near-zero concentrations (Barrie et al. 1988; Simpson et al. 2007). These  
179 phenomena are most commonly observed at Arctic coastal locations in March/April and attributed to bromine  
180 (halogen) sources linked to Arctic sea ice, coupled with stable surface temperature inversions (e.g. Figure 1;  
181 Hermann et al., 2019). Interestingly, Yang et al. (2020) and Huang et al. (2020) were able to explain major  
182 depletion events in a model study by introducing the wind-induced release of bromine from the snowpack.  
183 However, the models could not explain the depletion events observed at low wind speeds. Swanson et al. (2022)  
184 used the GEOS-Chem model to show that both blowing snow and the snowpack are important sources of bromine  
185 during the spring. Figure 2 shows the vertical extent of low O<sub>3</sub> episodes observed by lidar at Eureka in northern  
186 Canada. On May 7<sup>th</sup>, low O<sub>3</sub> concentrations were observed and back trajectories showed that air masses came in  
187 from the ice-covered Arctic Ocean and had been in contact with the surface multiple times during the previous 6  
188 days, whereas the concentrations were high on May 9, when air came down from the mountains located to the  
189 south (Seabrook and Whiteway, 2016). Peterson et al. (2018) showed that active halogen chemistry and related O<sub>3</sub>  
190 depletion can also occur up to 200 km inland over snow-covered tundra in Alaska. Simpson et al. (2018) reported  
191 high levels of bromine oxide (BrO) at Utqiagvik (previously known as Barrow, Alaska) occurring earlier in  
192 February in air masses originating from the Arctic Ocean polar night. Their findings suggest a dark wintertime  
193 source of reactive bromine (halogens) that could feed halogen photochemistry at lower latitudes as the sun returns.

194 In addition, whilst earlier studies proposed indirect evidence that O<sub>3</sub> and gaseous elemental mercury (Hg<sup>0</sup>) is  
195 removed by reaction with Br atoms (e.g. Skov et al. 2004; Skov et al. 2020; Dastoor et al. 2008), Wang et al.  
196 (2019) showed, for the first time, a direct connection between O<sub>3</sub> and Hg<sup>0</sup> with atomic bromine (Br) during O<sub>3</sub> and  
197 Hg<sup>0</sup> depletion episodes at Utqiagvik, on the north coast of Alaska (see Figure 3) where O<sub>3</sub> and Hg<sup>0</sup> are removed



198 in competing reactions with Br. Here, the Br/BrO ratio anti-correlates with O<sub>3</sub> concentrations and box modeling  
199 confirms that O<sub>3</sub> is removed by Br.

200 This result is significant since the main source of halogens in the Arctic is the release from refreezing snow and  
201 ice, snow blowing over sea ice, heterogeneous reactions of aerosol particles, and snowpack recycling (Petersen et  
202 al. 2016; Peterson et al., 2017, Wang et al., 2017; Yang et al. 2020). Burd et al. (2017) found a strong relationship  
203 between the end of the reactive bromine season and snowmelt timing. In the future, continued decreases in Arctic  
204 sea ice extent or the relative distributions of multi-year/seasonal sea-ice cover, coupled with increases in the length  
205 of the snow-free season over land could influence the magnitude and seasonality of O<sub>3</sub> sinks via changes in halogen  
206 fluxes or dry deposition fluxes to tundra/ocean rather than snow/ice surfaces.

### 207 3. AMAP models and simulations

208 To evaluate our process understanding of controls on the Arctic tropospheric O<sub>3</sub> budget and distribution, we  
209 evaluate a suite of model simulations. Twelve atmospheric models participated in this study; 7 chemical-transport  
210 models (DEHM, EMEP-MSC W, GEOS-Chem, MATCH, MATCH-SALSA, OsloCTM, WRF-Chem) and 5  
211 chemistry-climate models (CESM, CMAM, GISS-E2.1, MRI-ESM2, and UKESM1), with simulations of the years  
212 2014–2015 for comparisons to observations. All models used the same set of anthropogenic emissions called  
213 ECLIPSEv6b (AMAP 2022), though had different sources for fire, biogenic emissions, and meteorology (see  
214 Table S1). All participating models prescribe CH<sub>4</sub> concentrations based on box model results, which are, in turn,  
215 based on the ECLIPSEv6b anthropogenic CH<sub>4</sub> emissions, and various assumptions on natural CH<sub>4</sub> emissions  
216 (Olivié et al., 2021; Prather et al., 2012). Models then allow CH<sub>4</sub> to take part in photochemical processes. The  
217 participating models have varying degrees of spatial resolution and chemical complexity; air quality-focused  
218 models, such as DEHM, EMEP MSC-W, GEOS-Chem, MATCH, and WRF-Chem have detailed HO<sub>x</sub>-NO<sub>x</sub>-  
219 hydrocarbon O<sub>3</sub> chemistry, with speciated volatile organic compounds (VOCs), and secondary aerosol formation,  
220 and tend to run at higher resolution. The earth system models GISS-E2.1, MRI-ESM2, and UKESM1 also contain  
221 this level of tropospheric chemistry, though run globally at coarser resolution. Whereas, climate-focused models  
222 like CMAM, run at a coarse resolution and have simplified tropospheric chemistry in order to be able to run for  
223 long periods. For example, CMAM's tropospheric chemistry consists only of CH<sub>4</sub>-NO<sub>x</sub>-O<sub>3</sub> chemistry, with no  
224 VOCs.

225 As mentioned above, Arctic tropospheric O<sub>3</sub> is heavily influenced by imports from the stratosphere. The models  
226 vary, too, in their representation of the stratosphere. Only a subset of participating models have a fully simulated  
227 stratosphere. CMAM, MRI-ESM2, GISS-E2.1, OsloCTM, and UKESM1 contain relatively complete stratospheric  
228 O<sub>3</sub> chemistry (NO<sub>x</sub>, NO<sub>x</sub>, Cl<sub>x</sub>, Br<sub>x</sub> chemistry that controls stratospheric O<sub>3</sub>). Other models have a simplified  
229 stratosphere, such as GEOS-Chem which has a linearized stratospheric chemistry scheme (LINOZ, McLinden et  
230 al., 2000), and WRF-Chem which specifies stratospheric concentrations from climatologies. Finally, several  
231 models have no stratosphere or stratospheric chemistry at all (e.g., DEHM, and EMEP MSC-W). Most atmospheric  
232 models, including all of the models in this study, do not yet contain Arctic tropospheric bromine chemistry, and  
233 thus cannot simulate the surface-level bromine-driven O<sub>3</sub> depletion events that occur during spring. However,



234 there are research versions of some models which are starting to contain this chemistry (e.g., Parrella et al., 2012;  
235 Falk and Sinnhuber, 2018; Badia et al., 2021)

236 These same 12 model simulations were also evaluated against a different set of measurements in AMAP (2022)  
237 and Whaley et al. (2022). Those studies focused on many SLCF species over the Northern Hemisphere and  
238 generally reported model biases for the annual mean concentrations. They found that all models overestimated  
239 surface O<sub>3</sub> concentrations at mid-latitudes, but that there were both over- and underestimation in the Arctic.  
240 Particularly, models overestimated surface O<sub>3</sub> in the western Arctic (e.g., Alaska), particularly in the summertime,  
241 but were better able to simulate the surface O<sub>3</sub> seasonal cycle in the eastern Arctic (e.g., northern Europe). They  
242 also found that model biases were small throughout the free-troposphere when compared to remote measurements  
243 from the Tropospheric Emission Spectrometer (TES) satellite instrument.

244 In the next sections, these models are compared with observations of O<sub>3</sub> and its precursors either individually, or  
245 as the multi-model median (MMM) - whereby the median of all 12 atmospheric models is shown unless otherwise  
246 noted. The model output was selected from the model grid box that contains the latitude and longitude of the  
247 observation location without any spatial interpolation.

#### 248 **4. Arctic-wide tropospheric distributions from satellite data**

249 Despite the potential limitations of some satellite data products at high latitudes, several studies have exploited  
250 satellite observations to investigate tropospheric O<sub>3</sub> and precursor distributions and trends relevant to the Arctic.  
251 Pommier et al. (2012) presented IASI retrievals of 0-8 km and 0-12 km sub-column O<sub>3</sub> for the Arctic in spring and  
252 summer 2008. These showed widespread enhancements in spring-time (Mar-Apr) tropospheric O<sub>3</sub> column  
253 compared with summer (Jun-Jul), particularly over northeast Siberia, northern Canada and the Arctic Ocean.  
254 Generally, good agreement with in-situ aircraft profiles was demonstrated, but negative IASI biases were found  
255 compared with aircraft data in the lower troposphere, due to low thermal contrast in the Arctic boundary layer.  
256 Wespes et al., (2012) showed that IASI was able to detect enhancements in mid-latitude sourced O<sub>3</sub> enhancements  
257 during summer at the edge of the Arctic, but also showed a lack of sensitivity over snow and ice surfaces,  
258 potentially resulting in missing some O<sub>3</sub> enhancements. Sodemann et al. (2011) analyzed the cross-polar transport  
259 of a large pollution plume originating from Asia during the summer of 2008 using IASI CO retrievals. IASI was  
260 able to detect features and structures of the plume consistent with in-situ aircraft data.

261 Satellite observations are also useful in evaluating the sources and export of O<sub>3</sub> precursors from mid-latitude source  
262 regions and their subsequent transport to the Arctic. Tropospheric NO<sub>2</sub> columns measured from OMI have been  
263 used to detect enhancements and trends in NO<sub>x</sub> emissions due to gas flaring in high latitude (up to 67°N) areas of  
264 Russia and North America (Li et al., 2016). Assessment of a suite of chemical transport models using OMI  
265 tropospheric NO<sub>2</sub> columns for summer 2008 showed a potential overestimate in NO<sub>2</sub> over biomass burning regions  
266 in eastern Siberia, with lower biases over European and North American source regions, and model under-  
267 estimates over China (Emmons et al., 2015). A comparison of regional model-simulated tropospheric NO<sub>2</sub> columns  
268 with observations from the OMI satellite instrument suggests potential underestimates in anthropogenic NO<sub>2</sub>  
269 emissions over high latitude Siberia and the Russian Arctic (Thorp et al., 2021). Monks et al., (2015) exploited  
270 limited profile information from MOPITT CO retrievals to evaluate relationships between CO seasonal cycles in





271 the lower and upper troposphere over the Arctic and mid-latitude source regions. Atmospheric Infrared Sounder  
272 (AIRS) CO retrievals from 2007 to 2018 have been used to characterize atmospheric circulation patterns coincident  
273 with pollution enhancements during Arctic spring (Thomas et al., 2021), and IASI CO column measurements have  
274 been used to analyze transport pathways for Asian anthropogenic pollution to the Arctic (Ikeda et al., 2021). Osman  
275 et al. (2016) constructed three-dimensional ( $5^\circ \times 5^\circ \times 1$  km) gridded climatologies of CO via a domain-filling  
276 trajectory mapping technique based on MOZAIC-IAGOS in situ measurements of commercial aircraft flights.  
277 These climatologies agreed well using forward and backward trajectories ( $< 10$  % difference for most cases) and  
278 against vertical measurements from MOZAIC-IAGOS not included in the climatologies. These climatologies were  
279 compared with CO retrievals from MOPITT, small biases were found in the lower troposphere while differences  
280 of  $\sim 20$  % were found between 500 and 300 hPa, which declined throughout the study (2001-2012). Inter-annual  
281 variability in PAN retrieved by TES over Eastern Siberia for April 2006-2008 was documented by Zhu et al.,  
282 (2015), and it was shown to be largely controlled by boreal fire emissions at this time of year. More recently, PAN  
283 data from the TES instrument was used to help characterize Asian influence on exported PAN and downwind  $O_3$   
284 production (Jiang et al., 2016). A temperature-dependent high bias in TES PAN was found at cold temperatures  
285 over high latitudes.

286 In both Chapter 7 of the 2022 AMAP SLCF report (AMAP, 2022) and Whaley et al. (2022), data from satellite  
287 instruments, TES, ACE-FTS, and MOPITT are used to evaluate modeled  $O_3$ ,  $CH_4$ , and CO in the Northern  
288 Hemisphere. They showed that model biases for  $CH_4$  were small, though tended to be negative in the Arctic due  
289 to a lack of north-south gradient in the prescribed global distribution. Model biases were also negative for free-  
290 tropospheric  $O_3$ , however, it was by approximately the same amount that TES  $O_3$  retrievals have been shown to  
291 be biased high by Verstraeten et al. (2013). The ACE-FTS comparison for  $O_3$  showed good agreement but had  
292 higher model biases around 300-100 hPa in Whaley et al. (2022) and AMAP (2022). The MOPITT CO  
293 comparisons in AMAP (2022) showed that all models' CO are biased low over land in the mid-latitudes, but biased  
294 high over the oceans at lower latitudes. Monks et al. (2015) discussed that models had high biases in the outflow  
295 from Asia, and low biases north of there due to lack of transport. The Quennehen et al. (2016) study also suggested  
296 that summertime CO transport out of Asia is too zonal. This could explain some of the underestimations in the  
297 Arctic CO in the mid-troposphere.

## 298 **5. Arctic surface $O_3$ and precursors: seasonal cycles**

299 In the high Arctic, there is very little diurnal variation in surface  $O_3$ , most likely because the local and regional  
300 photochemistry is of limited importance most of the time and due to the 24-hour daylight during Arctic spring,  
301 summer and Autumn as well as the polar night during winter, see earlier. For High Arctic sites, the seasonal  
302 dynamics of  $O_3$  can be explained mostly by long-range transport and particularly in the winter and springtime,  
303 intrusion from aloft, see Figure 5a. Moving southwards to the Polar Circle a clearer diurnal pattern is evident  
304 caused both by the seasonal behavior of vertical mixing, deposition, transport, and local chemistry (references) as  
305 the stations on the Scandinavian peninsula, and Denali central Alaska.

306



## 307 **5.1 Surface Ozone**

308 Seasonal differences in the Arctic are important because of differences between the local meteorological  
309 conditions, as well as atmospheric transport, in the warm and the cold seasons and seasonal variations in O<sub>3</sub> sources  
310 and sinks. Surface O<sub>3</sub> at remote midlatitude sites with limited influence from local and regional anthropogenic O<sub>3</sub>  
311 precursor emissions have been found to frequently exhibit a characteristic seasonal cycle with peak values during  
312 spring and a minimum in the summer, while sites with high exposure to O<sub>3</sub> from anthropogenic precursors have  
313 summer time O<sub>3</sub> maxima (Monks 2000; Parrish et al. 2013, 2019; Gaudel et al., 2018). The spring maxima has  
314 been explained by stratospheric intrusions as well as enhanced photochemical formation during this period of the  
315 year. The summer minima, e. g. observed at the Mace Head site (Derwent et al., 1998, 2013, 2020), which is  
316 strongly influenced by marine air, appears to be explained by photochemical destruction in the absence of  
317 anthropogenic precursors. Seasonal cycles at Arctic stations are not extensively discussed in the literature, but it  
318 is evident that the halogen chemistry discussed above, most frequently observed at high Arctic coastal stations,  
319 leads to a significant reduction during the springtime (e.g. Oltman and Komhyr, 1986; Tarasick et al., 1995; Monks  
320 et al., 2015). Regarding the more southerly Arctic and near-Arctic sites, a latitudinal gradient has been observed  
321 in the timing of the spring O<sub>3</sub> maximum. Anderson et al. (2017) found that monthly mean observed near-surface  
322 O<sub>3</sub> concentrations at background sites in Sweden from 1990 to 2013 had a maximum in spring, but the most  
323 northerly stations experienced their maximum in April while the more southerly ones in May.

324 In order to get an overview of the annual O<sub>3</sub> cycles at different types of Arctic surface measurement sites, we have  
325 calculated the monthly medians and interquartile range for the period 2003-2019 for a series of sites. A map of the  
326 stations as well as their coordinates and elevation can be seen in Figure 4. Figure 5 illustrates the range of seasonal  
327 cycle behavior observed in the Arctic at different measurement sites and shows different seasonal cycles depending  
328 on location.

### 329 **5.1.1 High Arctic sites**

330 Figure 5a shows that the seasonalities in O<sub>3</sub> at Villum, Barrow/Utqiagvik, Alert, Tiksi and Eureka are similar:  
331 They have a local minimum in spring due to the occurrence of ODEs, a slight increase/recovery in June and a  
332 second minimum in July due to surface removal and photochemical degradation of O<sub>3</sub>. These stations are located  
333 at high latitude coastal sites close to sea level. During winter, O<sub>3</sub> reaches a maximum, due to an absence of  
334 photochemical degradation of O<sub>3</sub>, vertical mixing is suppressed during polar night since the Arctic boundary layer  
335 is often highly stratified, thus hampering removal by dry deposition (Esau and Sorokina, 2016).

### 336 **5.1.2 Near Arctic Circle sites**

337 The characteristic seasonal variations of surface O<sub>3</sub> measured at stations close to the Arctic Circle are shown in  
338 Figure 5b. The stations are Karasjok and Tustervatnet in Norway, Esrange in Sweden, Pallas in Finland and Denali  
339 in Alaska. The sites in Figure 5b, which are not influenced by ODEs, exhibit a yearly cycle that is more similar to  
340 lower latitude European stations at remote locations. Here, surface O<sub>3</sub> exhibits a late spring maximum which is  
341 attributed to photochemical production and transport of O<sub>3</sub> from the stratosphere (Monks, 2000). The largest  
342 differences between the stations are mainly found during the summer months, most likely due to the influence of  
343 local sources on photochemical O<sub>3</sub> production.



344 Kårvatn in Norway has an unusual behavior with an O<sub>3</sub> maximum in March, possibly due to the local conditions:  
345 The site often shows a pronounced diurnal cycle in O<sub>3</sub> due to the location at the bottom of a valley that causes  
346 strong inversions leading to an enhanced impact of dry deposition at night on surface O<sub>3</sub> (Aas et al., 2017).

347 Hurdal in Norway is included as an example of a more southerly Scandinavian non-Arctic station, which has an  
348 annual variation with a minimum in October while the more northerly stations have minima between July and  
349 September (Figure 5c), this difference may be explained by a stronger influence of local air pollution at Hurdal.  
350 At Hurdal, winter O<sub>3</sub> concentrations are particularly low, probably also in this case due to the influence of local  
351 emissions which in this period leads to the removal of O<sub>3</sub> by the reaction with NO.

### 352 5.1.3 Other sites: Inland high-elevation

353 Summit (located in the free troposphere on the Greenland Ice Sheet) is much less affected by bromine chemistry  
354 originating from sea ice or other low altitude processes than the coastal High Arctic sites (Huang et al. 2017).  
355 Consequently, the seasonal variation is different with a clear maximum in May, a minimum in September, the  
356 higher concentrations compared to other surface stations can be explained by the high sensitivity to stratospheric  
357 O<sub>3</sub> enriched air (Monks et al., 2015) at this high elevation (3211 masl) site. Short episodes of depletion have been  
358 reported (Brooks et al. 2011) but they do not appear to affect the monthly mean values substantially as shown in  
359 Figure 5c.

360 Zeppelin, although a high Arctic site, is located on a mountain ridge at 474 masl and thus experiences free  
361 tropospheric air masses more often compared to sea level sites. For this reason, it is less influenced by ODEs and  
362 consequently does not have an O<sub>3</sub> minimum in spring like the other high Arctic coastal stations (Figure 5c). That  
363 said, the occasional ODE has been reported there by Lehrer et al. (1997) and Ianniello et al. (2021).

364 We also note that surface O<sub>3</sub> can be influenced by local anthropogenic emissions such as shipping (e.g. Marelle et  
365 al., 2016, Aliabadi et al., 2015) or oil field emissions (McNamara et al., 2019). McNamara et al. (2019) discussed  
366 potentially important interactions between local anthropogenic NO<sub>x</sub> emissions from the Barrow settlement or the  
367 Prudhoe Bay oil extraction facilities in northern Alaska and snowpack (chlorine) chemistry leading to elevated  
368 concentrations of nitrogen-containing compounds (e.g. N<sub>2</sub>O<sub>5</sub>, HO<sub>2</sub>NO<sub>2</sub>), with implications for Arctic tropospheric  
369 O<sub>3</sub>. Therefore, while none of the Arctic sites currently exhibit summertime surface maxima due to photochemical  
370 production, as often observed in polluted locations further south, this may change in the future with increasing  
371 local anthropogenic emissions (e.g. Marelle et al. 2018).

372 He et al. (2016) measured O<sub>3</sub> and black carbon on a ship cruise to the Arctic Ocean (31.1°N to 87.7°N and 9.3°E–  
373 90°E to 168.4°W) from June to September 2012. Comparing the observed O<sub>3</sub> concentrations to those measured at  
374 Barrow showed no statistically significant differences, the authors suggest that coastal stations between July and  
375 September may be representative of the entire Arctic but this hypothesis requires further investigation. Indeed, our  
376 results show significant differences in the O<sub>3</sub> seasonal cycles at different Arctic locations depending on whether  
377 they were coastal, in-land, or high elevation.

378



## 379 5.2 Surface O<sub>3</sub> model evaluation

380 It has been found that halogen chemistry, stable boundary layers, and dry deposition explained differences between  
381 measured and modeled O<sub>3</sub> concentrations, as demonstrated by Kanaya et al. (2019) who performed measurements  
382 of CO and O<sub>3</sub> during several ship cruises in the Bering Sea and the Arctic Ocean in September (2012 to 2017).  
383 None of the models in our study contain surface halogen chemistry but they also display highly variable agreement  
384 in their surface O<sub>3</sub> seasonal cycles. Figure 6 shows the seasonal cycle from the models and observations averaged  
385 for 2014-15 at several Arctic observation locations. Since the models do not contain surface-level bromine  
386 chemistry, at locations like Alert and Barrow/Utqiagvik, they do not capture the springtime minimum in O<sub>3</sub>. Some  
387 models (e.g. UKESM1) greatly underestimate wintertime O<sub>3</sub>. This may be related to deficiencies in boundary layer  
388 mixing or an overly shallow boundary layer depth, resulting in the overly active titration of O<sub>3</sub> by NO near NO<sub>x</sub>  
389 emission sources and subsequent underestimation of Arctic surface O<sub>3</sub>. However, other model deficiencies could  
390 also play a role, including dry deposition and NO<sub>x</sub> lifetime. Indeed, Barten et al. (2021) found that overestimation  
391 of oceanic O<sub>3</sub> deposition can explain some differences between modeled and measured surface O<sub>3</sub> in the High  
392 Arctic. Some models in Figure 6 do not agree on the timing of the springtime peak, with CMAM, DEHM, and  
393 GISS-E2.1 peaking in April, and EMEP-MSC-W and MRI-ESM2 peaking in May/June. The same groupings of  
394 models display different O<sub>3</sub> behavior at the end of the year (October-December), with CMAM, DEHM, and GISS-  
395 E2.1 all correctly simulating an increase in O<sub>3</sub>, and EMEP-MSC-W and MRI-ESM2 having a decrease. All models  
396 agree better with observations and each other on summertime surface O<sub>3</sub> abundance at all locations, and on the  
397 full seasonal cycle at Summit, the high-elevation background location. The large range of modeled surface O<sub>3</sub> is  
398 similar to previous model studies (Shindell et al., 2008; Monks et al., 2015; Gaudel et al., 2018). Despite the large  
399 range in model performance, the overall average negative O<sub>3</sub> bias, and the seasonality in model bias at  
400 Barrow/Utqiagvik and Summit, are consistent with these previous studies. The comparisons highlight little change  
401 in the skill of models in simulating Arctic surface O<sub>3</sub> over the past decade.

402 These particular model simulations have been evaluated in Whaley et al. (2022), where they grouped all western  
403 Arctic (defined as lat > 60°N, and lon < 0°) and eastern Arctic (lat > 60°N, lon > 0°) O<sub>3</sub> measurements together, and  
404 showed the range in modeled and measured seasonal cycles for those two regions. That analysis included  
405 additional locations at lower latitudes, thus their results emphasized that some models overestimated summertime  
406 O<sub>3</sub> in the western Arctic. Otherwise, the results from that study are consistent with what we report here.

## 407 5.3 Ozone precursors

408 NO<sub>x</sub> monitors have been used at several Arctic sites but in a study at Zeppelin, it was shown that most of the NO<sub>x</sub>  
409 was in the form of the NO<sub>x</sub> reservoir species PAN (Beine et al., 1997; Beine and Krognnes, 2000). We evaluate and  
410 discuss PAN in Section 6.3 from aircraft measurements. There are only limited sources for NO<sub>x</sub> in the Arctic and  
411 the lifetime of NO<sub>x</sub> is in the order of a day. Whaley et al. (2022) evaluated surface NO<sub>x</sub> volume mixing ratios and  
412 found that these models underestimated surface NO<sub>2</sub> by -59% at low-Arctic latitudes that were mostly around  
413 60°N.

414 The dominant source for NO<sub>x</sub> is long-range transport of dominantly PAN (Beine and Krognnes; 2000), and  
415 particulate bound HNO<sub>3</sub> followed by reactivation in the Arctic by thermal decomposition and photoreduction



416 processes, respectively. Kramer et al. (2015) determined at Summit from July 2008 to July 2010 that PAN  
417 accounted for 295 ppt, and  $\text{NO}_x$  for 88 ppt. In a more recent study, Huang et al. (2017) found in the period July  
418 2008–June 2010, PAN and  $\text{NO}_x$  were maximum in spring at about 250 ppt and 25 ppt, respectively, and in summer  
419 75 ppt and 20 ppt, respectively. Beine and Krognes, (2000) measured PAN at Zeppelin Mountain between 1994  
420 and 1996. They found median values were lowest in summer at 89.4 ppt and highest in spring at 222.6 ppt.  $\text{HNO}_3$   
421 in the gas phase is in general very low (Wespes et al., 2012). Particulate bound nitrate – potentially a significant  
422 source of  $\text{NO}_x$  in the atmosphere and snow pack – is close to the detection limit in summer and up to 124.7 ng N  
423  $\text{m}^{-3}$  in winter e.g. at Villum (Nguyen et 2013).

424 In general, NMVOC concentrations in the Arctic are low and thus their photo-oxidation has only a limited impact  
425 on  $\text{O}_3$ . There is a series of studies dedicated to specific source regions and emission sources. There is one long  
426 term measurement study by Gautrois et al. (2003); studies focusing on long-range transport (Stohl, 2006; Harrigan  
427 et al., 2011), snowpack emissions (Boudries et al., 2002; Dibb and Arsenault, 2002; Guimbaud et al., 2002; Barret  
428 et al., 2011; Gao et al., 2012) and shipborne measurements (Sjostedt et al., 2012 and Mungall et al., 2017). The  
429 Gautrois et al. (2003) study reported long-term VOC concentrations for Alert, NU, they found yearly levels of  
430 ethane, propane and toluene are 1.7 ppbv, 0.6 ppbv and 26 pptv, respectively. For comparison, mixing ratios of  
431 ethane, propane, and toluene in China ranged from 3.7-17 ppbv, 1.5-20.8 ppbv, 0.4-11.2 ppbv, respectively  
432 (Barletta et al., 2005).

433 Pernov et al. (2021) measured organic  $\text{O}_3$  precursors online with a PTR-ToF-MS at Villum from April to October  
434 2018. Sources were apportioned with Positive Matrix Factorization During the late spring, the Arctic haze factor  
435 was a source of oxygenated VOCs (OVOCs) arising from long-range transport of anthropogenic emissions whilst  
436 during summer OVOCs and DMS originated from the Marine cryosphere factor. During autumn, the Biomass  
437 burning factor peaked in importance and was dominated by acetonitrile. The most abundant compound during the  
438 campaign was acetone with a mean mixing ratio of 0.6 ppbv, for benzene 0.027 ppbv and DMS 0.046 ppbv. In the  
439 future, local NMVOC emissions might increase from both natural and anthropogenic sources due to the retreating  
440 sea ice with more biological activity and more industrial activity and shipping affecting future levels of  $\text{O}_3$ .

441 Figure 7 shows the observed and simulated seasonal cycle of CO at Zeppelin and Utqiagvik/Barrow. Simulated  
442 CO ranges about 50 ppbv across models, and all models underestimate surface CO at these sites. The low model  
443 biases are dominated by the winter and spring months. The 2014-15 annual multi-model median (MMM) bias is -  
444 11% and -16% at Zeppelin and Barrow/Utqiagvik, respectively. Figure 7 shows that for the first 6 months of the  
445 year, the MMM is 20-30% too low, but that in the summer, the MMM is much closer to observations. These CO  
446 results are very similar to those found in previous multi-model studies (Shindell et al., 2008; Monks et al., 2015;  
447 Whaley et al., 2022). Similar to  $\text{O}_3$ , these results imply little change in the skill of models in simulating Arctic  
448 surface CO over the past decade. The modeled CO underestimations are well-reported in the literature, and  
449 attributed either to a lack of CO from combustion sources in the emission inventories (e.g., Kasibhatla et al., 2002;  
450 Pétron et al., 2002; Jiang et al., 2015), or to errors in OH, which impact the lifetime of CO (e.g., Monks et al.,  
451 2015; Quennehen et al., 2016). Indeed both may be at cause here, as the anthropogenic CO emissions from  
452 ECLIPSEv6b are lower than those in the CMIP6 emission inventory, neither of which have taken into account the  
453 reported discrepancies from top-down emissions studies (Kasibhatla et al., 2002; Pétron et al., 2002; Jiang et al.,



454 2015, Miyazaki et al., 2020). Monks et al. (2015) showed that models with lower global mean OH concentrations  
455 produced smaller underestimates in Arctic surface CO and that models with larger underestimates in CO over mid-  
456 latitude source regions also had larger underestimates in Arctic CO. Emmons et al. (2015) showed that the models  
457 with larger tropospheric OH also had higher photolysis rates of O<sub>3</sub> to O<sup>1D</sup> and that there was also some relationship  
458 between higher photolysis rates and lower cloud cover fraction in some models. Previous multi-model results have  
459 also shown that variability in model water vapour abundance in the Arctic appeared to be the leading driver of  
460 model variability in OH, despite being much less important at lower latitudes (Monks et al., 2015). Evaluating OH  
461 and water vapour is unfortunately beyond the scope of our study.

462 Methane has more than doubled since preindustrial times (from 0.8 ppmv to 1.8 ppmv) and the photooxidation of  
463 methane in the presence of NO<sub>x</sub> is a source of O<sub>3</sub>. Thawing permafrost and release from organic deposits in shallow  
464 Arctic Ocean waters in a warmer climate presents a new source of methane (Isaksen et al. 2014). The models of  
465 this study prescribed CH<sub>4</sub> concentrations, including their increasing trend, and they were found to have a small  
466 bias of ~2% in Whaley et al. (2022) compared to surface and satellite measurements. Going forward, models are  
467 starting to simulate CH<sub>4</sub> explicitly from emissions, and this will be important for simulating future changes in  
468 Arctic tropospheric chemistry.

## 469 6. Vertical distributions of O<sub>3</sub> and precursors in the Arctic

470 Observations and models have both demonstrated extensive layering of pollution signatures in the Arctic  
471 troposphere vertical profile, associated with varying air mass origins with altitude (Zheng et al., 2021; Willis et  
472 al., 2019). Large-scale isentropic transport pathways result in air masses from warmer more southerly latitudes  
473 being imported into the Arctic upper troposphere, while emissions from cooler northerly latitudes enter the Arctic  
474 near the surface and in the lower troposphere (Stohl, 2006). The presence of the Arctic dome during winter  
475 essentially shuts off access to the Arctic surface to air mass import from southerly mid-latitudes, while it facilitates  
476 efficient low-level transport of emissions from Northern Eurasia and Russia to the Arctic surface, giving rise to  
477 the well-known Arctic haze (Shaw, 19995). In practice, this large-scale dynamical control on long-range transport  
478 to the Arctic gives rise to a well-characterized vertical dependence of source region sensitivities for O<sub>3</sub> and  
479 precursors through the Arctic troposphere, where emissions from South and East Asia have the most influence in  
480 the Arctic upper troposphere, emissions from North America have the most influence in the Arctic mid-  
481 troposphere, and northern Eurasian and Russian emissions dominate at the surface (in addition to local influences)  
482 (Wespes et al., 2012; Monks et al., 2015). As mentioned in Section 1, this vertical layering and changes in the  
483 efficacy of O<sub>3</sub> radiative forcing with altitude has implications for the sensitivity of Arctic tropospheric O<sub>3</sub> forcing  
484 to regional emission perturbations.

485 Despite evidence for extensive vertical layering in the Arctic troposphere, and the potential for highly varying  
486 source contributions with altitude, aside from a limited set of regular O<sub>3</sub> sonde profiles, there is a severe lack of  
487 observations available on the vertical distribution of O<sub>3</sub>, and particularly its precursors, in the Arctic troposphere.  
488 There is an especially poor constraint on seasonal and interannual variability in O<sub>3</sub> precursor profiles. In this  
489 section, we make use of available vertical profile measurements of O<sub>3</sub> and its precursors to document our  
490 understanding of Arctic tropospheric O<sub>3</sub> profiles, and to evaluate model-simulated vertical profiles of O<sub>3</sub> and  
491 precursors.



## 492 6.1 Ozonesondes

493 Ozone soundings provide a long-term record of Arctic O<sub>3</sub> through the depth of the troposphere. Since 1966, weekly  
494 soundings have been available at Resolute and since the 1980s regular soundings, typically once a week, have  
495 been available from 6 stations north of 60°N (Figure 4, Table S.2). All of these stations are located in the sector  
496 95°W to 27°E meaning that regular soundings are lacking in a large sector of the Arctic. The measurements are  
497 conducted using the balloon-borne Electrochemical Concentration Cell (ECC) ozonesondes, typically reaching an  
498 altitude of about 30 km. Random uncertainties in tropospheric measurements are about 5%, and biases reported  
499 from field and laboratory comparisons to UV reference photometers are 1.0±4.4% in the lower troposphere and  
500 5.3±4.4% in the upper troposphere (Tarasick et al., 2019b). Mean observed concentrations have a minimum close  
501 to the surface and then gradually increase throughout the troposphere by about 50% and then increase sharply  
502 going into the upper troposphere and lower stratosphere (Figure 8 and Figure S.1-2). Observed seasonal cycles in  
503 the Arctic troposphere generally show a maximum in spring and summer and a minimum in fall and winter (Paper  
504 2).

505 Christiansen et al. (2017) examined long-term ozonesonde records at 9 Arctic stations reporting consistent seasonal  
506 cycles as a function of altitude between sites with later maxima in the mid-troposphere compared to the surface  
507 layers and upper troposphere.

## 508 6.2 Model evaluation against ozonesondes

509 Figure 8 shows a comparison of the ozonesonde measurements at Eureka to the simulations from the 12  
510 participating models for the annual and seasonal averages for the years 2014-15. In the supplement (Figure S.2),  
511 model-measurement comparisons at other Arctic locations are shown. Generally, the models are highly variable,  
512 ranging +/-50% of the measured O<sub>3</sub> profiles at most seasons and locations. However, the MMM performs well and  
513 is within +/-8% throughout most of the troposphere. However, all models, except UKESM1, have a bulge with a  
514 high model bias around 300-400 hPa, which is at or near the tropopause, implying that most models simulate the  
515 tropopause height too low (having larger stratospheric O<sub>3</sub> concentrations appearing too low in altitude). This results  
516 in a positive bias of about 20% for the MMM around the tropopause. This feature in models was also reported in  
517 AMAP (2015), where model biases were particularly large at Ny Alesund and Summit. They associated those with  
518 differences in the transport of air masses from the stratosphere. This issue will have an impact on estimating the  
519 tropospheric O<sub>3</sub> burden, which is a common climate diagnostic (e.g., Griffiths et al., 2021).

520 At Alert, there are both surface and ozonesonde measurements, and we find that the results in the lowest levels of  
521 the Alert ozonesonde comparisons (Figure S.1) are consistent with the model biases found in Figure 8 in that both  
522 show the models underestimating winter and fall O<sub>3</sub>, overestimating spring, and matching well with observations  
523 in the summer at this location.

524 Note that the models' monthly average O<sub>3</sub> values were used in this comparison, which does not match the time of  
525 day and day of the week as the ozonesonde measurements. However, when a careful time-matching to 3-hourly  
526 model output is carried out, the general features of the model biases remain the same (Figure S.2), likely because  
527 of the lack of a strong diurnal cycle in Arctic O<sub>3</sub> and its relatively long lifetime in the free troposphere.



528 The results of this model evaluation of the Arctic O<sub>3</sub> vertical profiles are consistent with Whaley et al. (2022),  
529 which compared the same model simulations to TES O<sub>3</sub> retrievals throughout the troposphere at lower Arctic  
530 locations (~60-70 °N). They found models to be biased low (around -10%), though the TES measurements have  
531 been shown to be biased high by about the same amount (+13% bias in TES measurements reported in Verstraeten  
532 et al., (2013)). They also saw a small positive shift in the model bias profile around 300 hPa as well. Finally, the  
533 Whaley et al. (2022) study included O<sub>3</sub>, NO<sub>x</sub>, CH<sub>4</sub>, and CO comparisons to the Atmosphere Chemistry Experiment  
534 (ACE)-Fourier Transform Spectrometer (FTS) satellite instrument, and those results also implied, independently,  
535 that the modeled tropopause heights are too low.

### 536 **6.3 Vertical distribution of O<sub>3</sub> precursors**

537 Intensive field measurement campaigns using aircraft provide the most detailed observational constraint on vertical  
538 profiles of tropospheric O<sub>3</sub> precursors in the Arctic. While these datasets tend to provide excellent spatial and  
539 temporal resolution measurements on a wide range of species, they are episodic in nature, often covering only a  
540 period of a few days to several weeks, flying in specific regions of the Arctic and often targeting specific layers or  
541 plumes. For example, Ancellet et al. (2016) examined aircraft, lidar and ozonesonde data over Canada and  
542 Greenland during the summer of 2008 POLARCAT campaigns (Law et al., 2014). This study showed clear  
543 latitudinal and longitudinal variations in the origins of sampled air masses based on back trajectories and O<sub>3</sub>-  
544 potential vorticity (PV) correlations. While downward transport of O<sub>3</sub> was important over Greenland, air masses  
545 with higher O<sub>3</sub> were attributed to North American boreal fires over Canada. Transport of polluted air masses from  
546 mid-latitudes also contributed, for example from Asia north of 80 °N.

547 The airborne NASA Atom (Atmospheric Tomography) mission (Wofsy et al., 2018) has undertaken extensive  
548 surveying of the global troposphere. This includes repeated vertical profile measurements between 60 °N and 90  
549 °N providing useful insights into the variation of O<sub>3</sub> and its precursors through the depth of the Arctic troposphere  
550 at different times of the year. Figure 9 shows these mean results and their standard deviation on the left-side panels,  
551 while the equivalent MMM results are on the right-side panels. The models' monthly mean results went into the  
552 MMM calculation and the standard deviation from the models is shown.

553 The results show that near-surface NO<sub>2</sub> is greatly enhanced during winter, associated with a longer NO<sub>2</sub> lifetime  
554 and accumulation of pollution in the Arctic haze. The MMM simulates the surface NO<sub>2</sub> increase and the seasonality  
555 of the NO<sub>2</sub> profiles reasonably well. However, generally, the modeled NO<sub>2</sub> is biased low in the tropospheric profile,  
556 having average values of about 15 pptv in the 2-6 km range, whereas the measurements are about 25 pptv on  
557 average. This underestimate is consistent with that found at the surface in Whaley et al. (2022). PAN is also  
558 enhanced at the surface in the winter and can thermally decompose in the spring and summer to release NO<sub>x</sub>. The  
559 MMM generally overestimates PAN (Figure 9c-d) and does not simulate the same shape in vertical profiles. For  
560 example, models are not able to simulate the wintertime surface level increase in PAN, and they have the inverse  
561 shape in April/May than the observed profile. The best agreement is in summertime PAN (July-Aug), when the  
562 MMM vertical profile better matches that of the observations. The underestimate of NO<sub>x</sub> and the lack of winter  
563 surface increases in PAN by the models may be a reason why the wintertime surface O<sub>3</sub> concentrations in Section  
564 5.2 and Figure 5 were underestimated. That said, it is possible that the NO<sub>x</sub> measurements are biased high and the  
565 PAN measurements are biased low due to thermal degradation in the sample line.





566 In line with ozonesonde data and previous airborne campaigns (AMAP, 2015), ATom profiles also demonstrate a  
567 springtime enhancement in  $O_3$  extending through the troposphere, with evidence of stratospheric influence in the  
568 upper troposphere and lower  $O_3$  in the summertime lower troposphere. The models capture that springtime  $O_3$   
569 enhancement as well. Summer enhancements in  $O_3$  precursors, such as CO and PAN in the mid-troposphere, were  
570 also observed associated with the import of forest fire and anthropogenic emissions from lower latitudes, as also  
571 seen during POLARCAT in 2008. The models capture this feature for PAN, but less so for CO. Indeed, most  
572 models underestimate CO. The annual mean, MMM bias for surface CO in the northern hemisphere has been  
573 reported to be -30% (Whaley et al., 2022). Figure 9 shows that below the tropopause, modeled  $O_3$  is actually close  
574 to observed  $O_3$ , despite the significant MMM biases for CO,  $NO_x$ , and PAN. Around the tropopause, the aircraft  
575 data show the same issue that the ozonesonde data did – that models overestimate  $O_3$  significantly near the  
576 tropopause.

## 577 7. Conclusions

578 Recent research on Arctic tropospheric  $O_3$  has resulted in improvements to our understanding of this pollutant and  
579 GHG in the rapidly changing and sensitive Arctic environment. We have shown in this study that Arctic surface  
580  $O_3$  seasonal cycles are different depending on whether sites are near the coast, inland, or at high elevation. Coastal  
581 sites have springtime minima due to halogen chemistry causing ODEs and show a maximum during the winter.  
582 The inland, near-Arctic circle locations have quite consistent seasonal cycles, with maxima in April and minima  
583 in August. While the high-elevation sites, less influenced by halogen chemistry than coastal locations, are more  
584 variable; Summit has a later maximum (May), and minimum (September), while Zeppelin has an earlier maximum  
585 (March) and minimum (July).

586 Despite model development that has occurred since the 2015 AMAP assessment report on ozone (AMAP, 2015)  
587 to add processes, improve parameterizations, increase resolution, etc, the resulting performance of the models  
588 remains more or less the same in terms of model variability and biases compared to measured  $O_3$  and  $O_3$ -precursor  
589 species in the Arctic. Model results for CO would improve if CO emissions from combustion were increased, as  
590 suggested in the literature. It would also be useful to compare modeled OH in the Arctic, but that was beyond the  
591 scope of this study. However, as Arctic  $O_3$  is limited by  $NO_x$  availability, improvements to CO may not have a  
592 large effect on  $O_3$ . Improvements to modeled PAN and  $NO_x$  are needed, however, sensitivity studies to determine  
593 the cause of the model biases will be required to improve model performance for those species. For surface  $O_3$   
594 distributions in the Arctic, models simulate background levels reasonably well (e.g., at the high-elevation location  
595 of Summit), but surface bromine/halogen chemistry needs to be included to simulate springtime surface  $O_3$  at  
596 coastal Arctic locations (e.g., Villum, Alert, and Utqiagvik). Except near the tropopause, models simulate  $O_3$   
597 throughout the vertical profile well, with the MMM performing best at +/- 8% depending on the location and  
598 altitude in the troposphere. Attention to improving the height of the modeled tropopause and/or the stratosphere-  
599 tropospheric exchange is still required since downward transport of high stratospheric  $O_3$  concentrations is causing  
600 model biases around 6 to 8 km (400 to 300 hPa) to be significantly large (>20%).

601 While they are logistically challenging, additional  $O_3$  measurements in the Arctic, such as  $O_3$  deposition  
602 measurements, observations of stratospheric-tropospheric exchange, and  $O_3$  concentrations in the Siberian Arctic,  
603 together with long-term measurements of  $O_3$  precursors, would be particularly helpful to improve our



604 understanding and modeling capabilities. This is particularly important as climate change alters the chemistry and  
605 dynamics of tropospheric O<sub>3</sub> in the future.

#### 606 **Author contributions**

607 CHW, KSL, JLH, HS, SRA, JL, and JBP wrote the manuscript and created Figures 3-9. RYC, JF, and XD provided  
608 the GEOS-Chem model output. JF, ST, and DT edited and provided comments on the manuscript. JHC provided  
609 the DEHM model output. GF, UI, and KT provided the GISS-E2.1 model output. MG and ST provided the EMEP-  
610 MSCW model output. KSL, JCR, TO, and LM provided the WRF-Chem model output. MD and NO provided the  
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#### 615 **Competing interests**

616 At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics. The  
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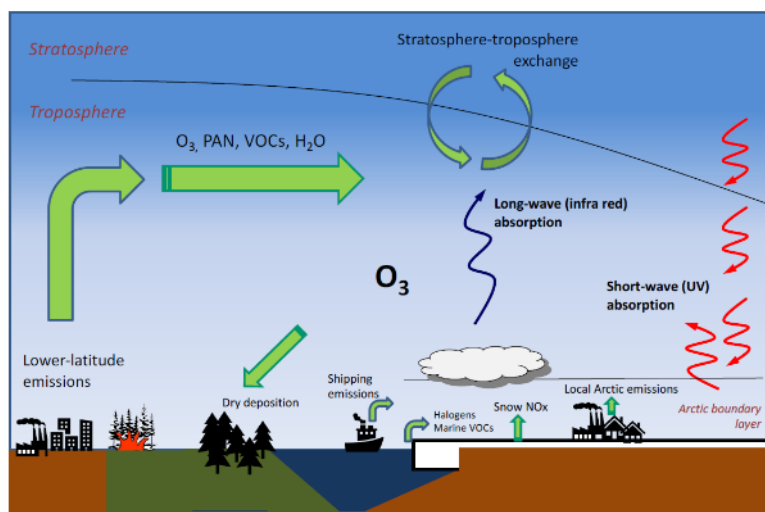
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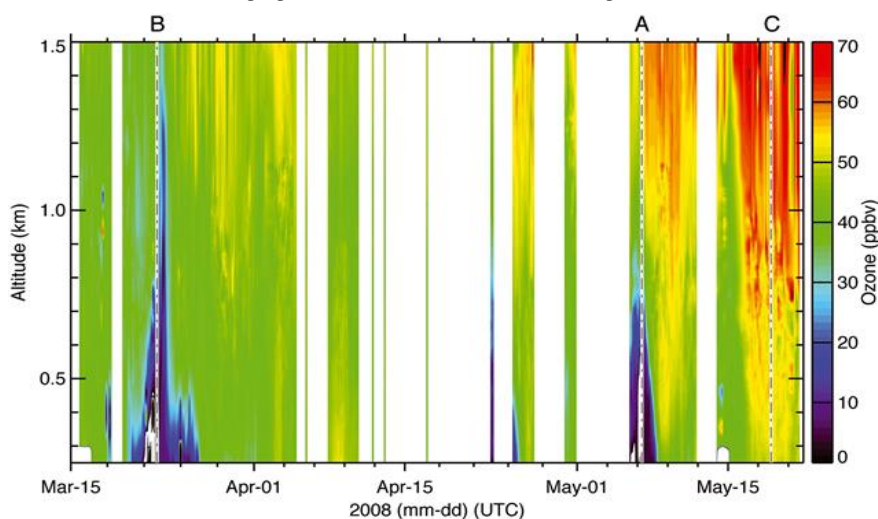
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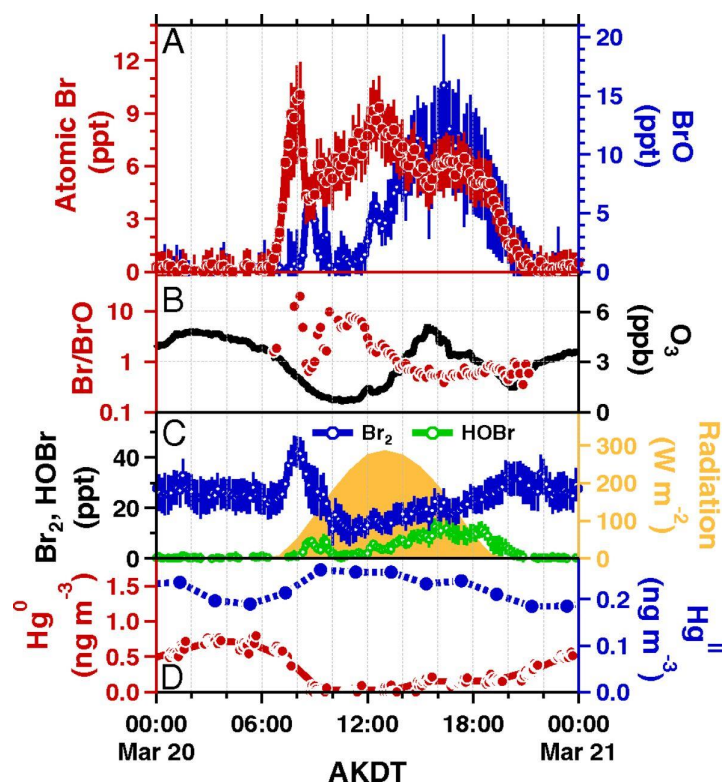


1101  
1102 **Figure 1:** Schematic of Arctic tropospheric O<sub>3</sub> sources, sinks, and relevant processes.



1103  
1104 **Figure 2:** Ozone lidar measurements from Eureka in the spring of 2008 showing effects of large-scale  
1105 meteorology including low O<sub>3</sub> in the lower troposphere when air masses originate from the north over the Arctic  
1106 Ocean and enhanced O<sub>3</sub> during downward transport into the Arctic boundary layer when the airflow was from  
1107 the south over mountains. From Figure 3 in Seabrook and Whitway (2016), *JGR Atmospheres*, vol. 121, Issue:  
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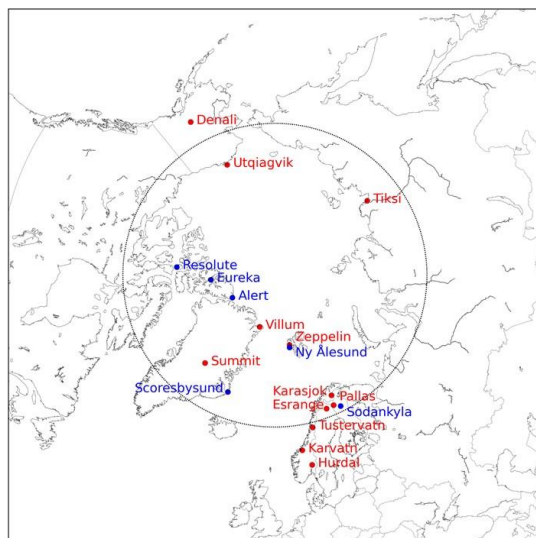
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1111 **Figure 3:** Time series at Uqiagvik on 20 March 2012 of measured (A) atomic bromine (Br) and bromine  
1112 monoxide (BrO), (B) Br/BrO ratios and O<sub>3</sub>. Error bars represent propagated measurement uncertainties. Figure  
1113 based on Wang et al. (2019, PNAS). (EPS figure provided for the report). From Figure 2 in Wang et al. (2019),  
1114 PNAS, vol. 116, no. 29, pages 14479-14484, Copyright (2019) National Academy of Sciences.

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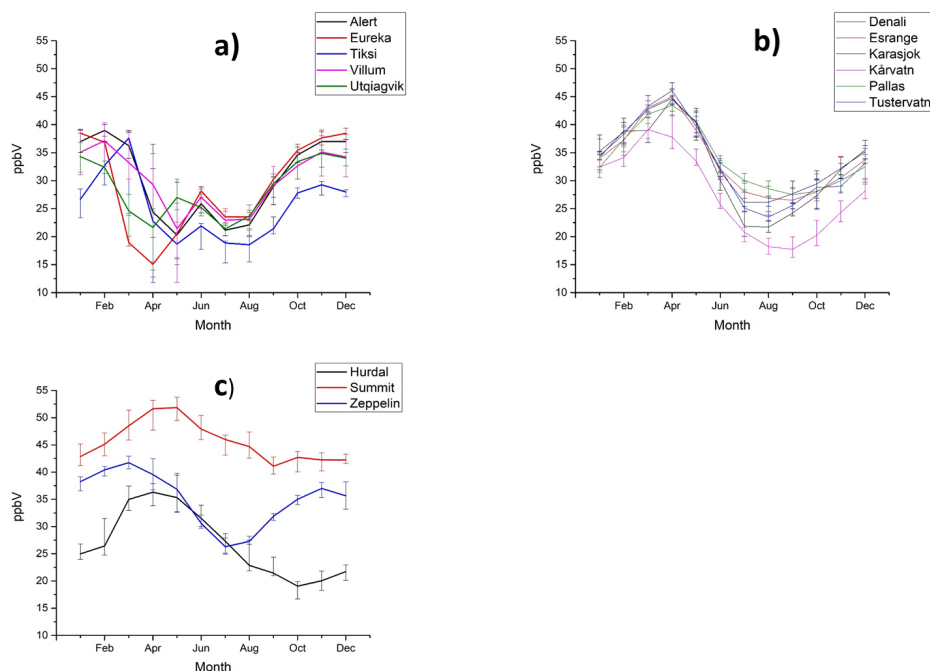


Name	Longitude	Latitude	Elevation (msl)
Alert	-62.33	82.50	66
Denali	-151.19	63.11	660
Esrange	21.07	67.88	475
Eureka	-86.4	80.1	83
Hurdal	11.07	60.44	300
Karasjok	25.22	69.47	333
Karvatn	8.88	62.78	210
Pallas	24.25	67.97	565
Summit	-38.48	72.57	3211
Tiksi	128.9	71.6	10
Tustervatn	13.87	65.83	439
Utqiagvik	-156.61	71.32	11
Villum	-16.67	81.60	20
Zepelin	11.89	78.91	474
Ny Alesund	11.49	78.51	
Resolute	-94.82	74.68	
Scoresbysund	-21.97	70.48	
Sodankyla	26.65	67.37	

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1117 **Figure 4.** Map of the surface (red) and ozonesonde (blue) sites, cited in the present study, with coordinates and  
 1118 elevation. Eureka and Alert are both surface and soundings sites. ‘Utqiagvik’ was formerly called ‘Barrow’.

1119 The Arctic Circle at 66.55° N is also shown in the figure for reference.

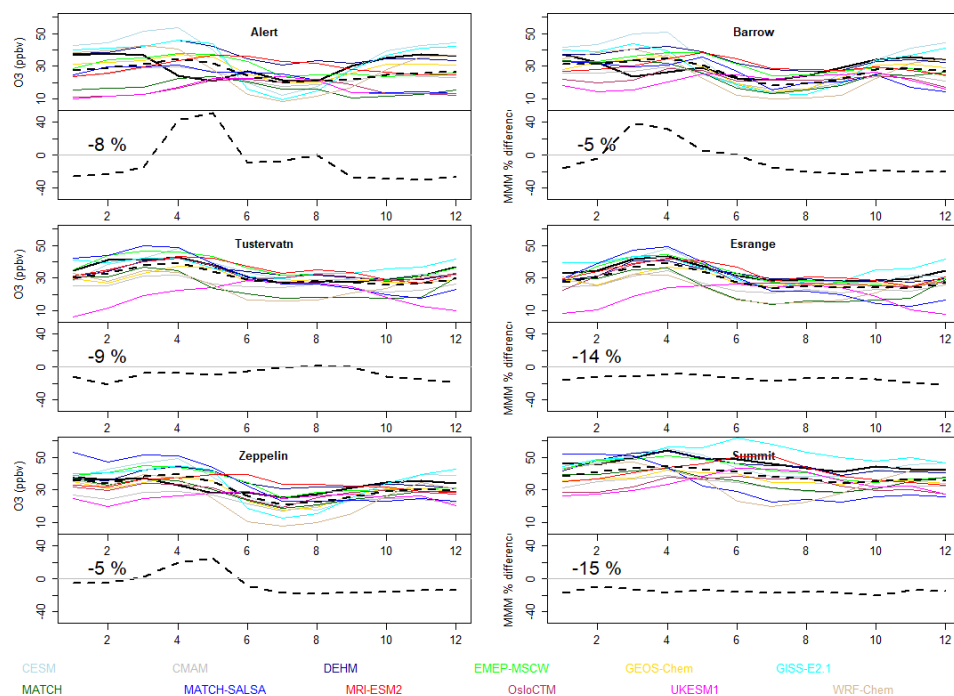


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1121 **Figure 5:** Seasonal behavior of surface O<sub>3</sub> at selected Arctic stations that are representative of a) coastal high  
 1122 Arctic b) near Arctic Circle and c) inland and high-elevation sites. Monthly medians are calculated for the period  
 1123 2003 to 2018. Data were not available for Villum and 2004 and 2013-2015 for Alert. The  
 1124 error bars show upper (75%) and lower (25%) quartiles.



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1127 **Figure 6:** Arctic surface O<sub>3</sub> by month; seasonal cycle model comparisons. Top row: coastal high-Arctic sites;

1128 middle row: near-Arctic circle sites; bottom row: high elevation sites. The solid black line is the observed O<sub>3</sub>

1129 monthly means, and the dashed black line is the multi-model median. Bottom row: sub-panels show the MMM

1130 % difference [(MMM - measurements)/measurements\*100].

1131 \*Note model results are from the 2014-15 mean. When available, the same years are used for the observations.

1132 However, Alert did not have data for 2014-15, so its most recent years were used: 2010-2013. Summit had 2014,

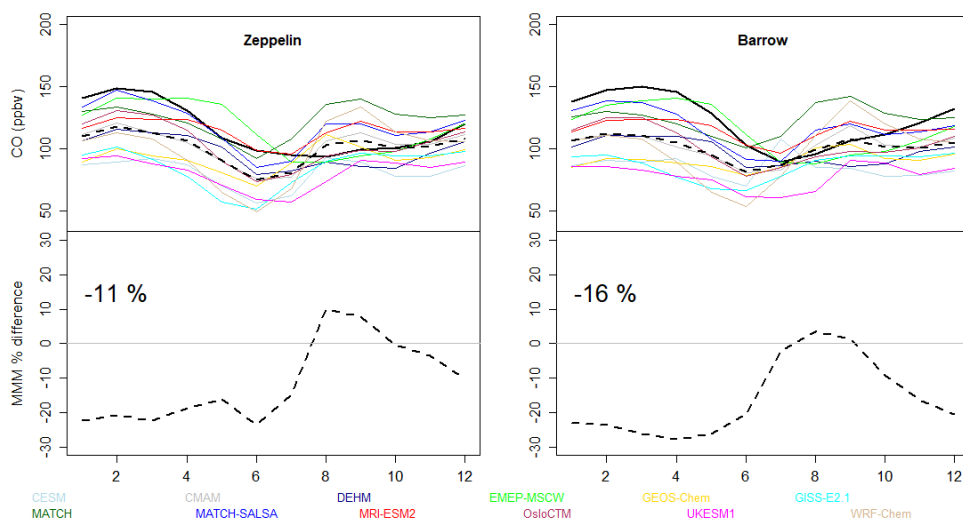
1133 but only 1 month in 2015, so its 2013-2015 data were used.

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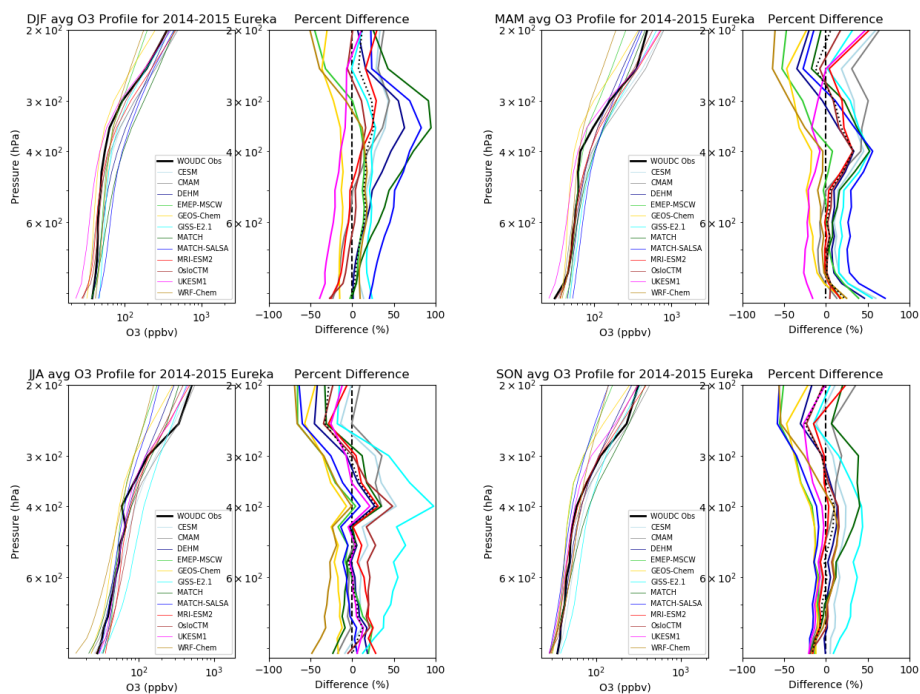
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1138 **Figure 7:** Arctic surface CO by month; seasonal cycle model comparisons. The solid black line is the observed  
1139 CO monthly means, and the dashed black line is the multi-model median (MMM). Bottom panels show the  
1140 MMM % difference  $[(\text{MMM} - \text{measurements})/\text{measurements} * 100]$ .

1141 \*Note model results are from the 2014-15 mean. When available, the same years are used for the observations.

1142 However, for Zeppelin observations are the mean of 2013-14.

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**Figure 8:** Comparison between observed (thick black line on left panels) and AMAP models' (colored lines) O<sub>3</sub> seasonal averages for 2014-15 at Eureka, NV, Canada. These use monthly mean model output. On each right panel, the dotted black line is the MMM, and the dashed black line shows zero bias for reference. See supplement (Figure S.1) for the rest of the ozonesonde locations, and a sample comparison done with 3-hourly model output (Figure S.2).

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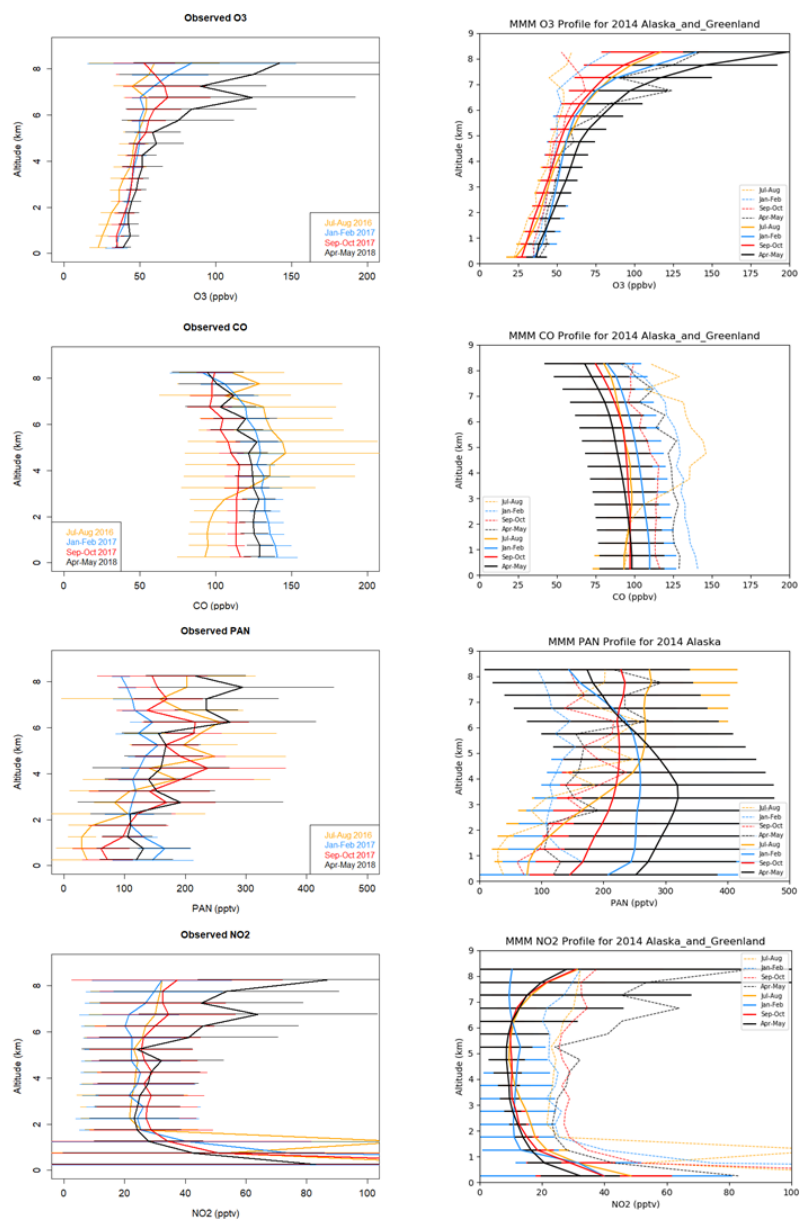
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1162 **Figure 9:** Mean vertical profiles of O<sub>3</sub>, CO, PAN and NO<sub>2</sub> (**left**) measured in Alaska and Greenland from the  
1163 NASA ATom missions during summer 2016, winter 2017, autumn 2017 and spring 2018 (horizontal lines  
1164 indicate 1 standard deviation spread around mean values at each altitude. (**right**) the MMM for the years 2014-  
1165 15 (with the MMM standard deviation as horizontal lines). The observations appear as dashed lines in the right  
1166 panels, for ease of comparing to the MMM.