Rapid O_3 assimilations – Part 2: tropospheric O_3 changes accompanied by declines in NO_x emissions in the US and Europe in 2005-2020

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Abstract

Tropospheric nitrogen dioxide (NO_2) concentrations have declined dramatically over the United States (US) and Europe in recent decades. Here we investigate the changes in surface and free tropospheric O_3 accompanied by NO_2 changes over the US and Europe in 2005-2020 by assimilating the Ozone Monitoring Instrument (OMI), and US Air Quality System (AQS) and European AirBase network O_3 observations. The assimilated O_3 concentrations demonstrate good agreement with O_3 observations: surface O_3 concentrations are 41.4, 39.5 and 39.5 ppb (US) and 35.3, 32.0 and 31.6 ppb (Europe); and tropospheric O_3 columns are 35.5, 37.0 and 36.8 DU (US) and 32.8, 35.3 and 36.4 DU (Europe) in the simulations, assimilations and observations, respectively. We find overestimated summertime surface O_3 concentrations over the US and Europe, which resulted in a surface O_3 maximum in July-August in simulations in contrast to April in observations. Furthermore, our analysis exhibits limited changes in surface O_3 concentrations, i.e., decreased by -6% over the US and increased by 1.5% over Europe in 2005-2020. The surface observation-based assimilations suggest insignificant changes in tropospheric O_3 columns: -3.0% (US) and 1.5% (Europe) in 2005-2020. While the OMI-based assimilations exhibit larger decreases in tropospheric O_3 columns, -12.0% (US) and -15.0% (Europe) in 2005-2020, the decreases mainly occurred in 2010-2014, corresponding to the reported slowed declines in free tropospheric NO_2 since 2010. Our analysis thus suggests limited impacts of local emission declines on tropospheric O_3 over the

32 US and Europe and advises more efforts to evaluate the possible contributions of natural

33 sources and transport. The discrepancy in assimilated tropospheric O_3 columns further

34 indicates the possible uncertainties in the derived tropospheric O_3 changes.

35

1. Introduction

37 The successful emission regulations employed in the United States (US) and Europe

38 (Crippa et al., 2016; EPA, 2017) have led to dramatic decreases in anthropogenic NO_x

39 emissions (Di et al., 2020; Macdonald et al., 2021; Jiang et al., 2022). As an important air

40 pollutant, tropospheric ozone (O_3) is produced when volatile organic compounds (VOCs) are

41 photochemically oxidized in the presence of nitrogen oxides (NO_x). As a major precursor of

42 tropospheric O_3, decreases in surface nitrogen dioxide (NO_2) concentrations, driven by declines

43 in NO_x emissions, have led to marked decreases in surface O_3 concentrations over the US and

44 Europe in recent decades. For example, Chen et al. (2021) found a decrease in surface O_3

45 concentrations from approximately 60 to 45 ppb over the US in 1990-2019; Seltzer et al. (2020)

46 exhibited a decreasing trend of surface O_3 by approximately 0.8 ppb yr^{-1} over the US in 2000-

47 2015; and Yan et al. (2018) found a decreasing trend of surface O_3 concentrations by

48 approximately 0.32 $\mu g/m^3/y$ over Europe in 1995-2014.

49 While NO_x emissions are declining, the shift of NO_x sources from power generation to

50 industrial and transportation sectors has led to diminishing effects on NO_x emission controls

51 (Jiang et al., 2022). Furthermore, recent studies have demonstrated a slowdown in tropospheric

52 NO_2 column declines with respect to surface NO_2 concentrations over the US since

53 approximately 2010 (Jiang et al., 2018; Laughner and Cohen, 2019; Qu et al., 2021). Jiang et

54 al. (2022) further indicated a slowdown of declines in tropospheric NO_2 columns with respect

55 to surface NO_2 concentrations over both the US and Europe. Unlike surface O_3, which is

56 strongly affected by local emissions, free tropospheric O_3 is more susceptible to the influences

2

57 of free tropospheric sources and sinks, long-range transport, and stratospheric intrusion (Jiang

58 et al., 2015; Xue et al., 2021; Trickl et al., 2020). The different trends in surface and free

59 tropospheric NO_2 may thus result in different changes in surface and free tropospheric O_3 over

60 the US and Europe.

61   A single O_3 tracer mode (tagged-O_3) of the GEOS-Chem model was developed in the

62 companion paper (Zhu et al., 2023) and was combined with Ozone Monitoring Instrument

63 (OMI) and surface O_3 observations in China in 2015-2020 via a sequential Kalman filter (KF)

64 assimilation system (Tang et al., 2022; Han et al., 2022). The rapid O_3 assimilation capability

65 with approximately 91-94% reductions in computational costs (Zhu et al., 2023) provides a

66 new opportunity to extend atmospheric O_3 observations and mitigate the influence of

67 uncertainties in physical and chemical processes (Li et al., 2019; Chen et al., 2022) and

68 emission inventories (Zheng et al., 2017; Jiang et al., 2022). As the second part of this work,

69 we assimilate OMI and US Air Quality System (AQS) and European AirBase network O_3

70 observations in this work to constrain tropospheric O_3 in the US and Europe in 2005-2020 with

71 a 0.5°×0.625° horizontal resolution. A comparative analysis by assimilating satellite and

72 surface O_3 observations is useful for better characterization of O_3 changes in the surface and

73 free troposphere. Furthermore, this analysis helps evaluate the long-term performance of the

74 GEOS-Chem model in simulating tropospheric O_3 and can provide new insights into

75 tropospheric O_3 changes accompanied by the reported changes in tropospheric NO_2.

76   This paper is organized as follows: in Section 2, we provide descriptions for the AQS,

77 AirBase and OMI O_3 observations and the single O_3 tracer simulation and assimilation system

78 used in this work. We refer the reader to the companion paper (Zhu et al., 2023) for more details

79 about the atmospheric O_3 observations and the development and performance of the single O_3

80 tracer assimilation system. Tropospheric O_3 changes in the US and Europe in 2005-2020 are

81 demonstrated in Section 3 by assimilating atmospheric O_3 observations. As shown in Fig. 1,

82   five regions (i.e., Great Lakes (#1), Northeast US (#2), West Coast (#3), Middle US (#4) and

83   Southeast US (#5)) are defined within the US domain, and five regions (i.e., Britain (#1),

84   Central EU (#2), Western EU (#3), Iberian Peninsula (#4) and Apennine Peninsula (#5)) are

85   defined within the European domain based on anthropogenic NO_x emissions in 2015. Regions

86   #1-3 (US) and regions #1-2 (Europe) are defined as highly polluted regions by excluding grids

87   with low and medium anthropogenic NO_x emissions. Tropospheric O_3 changes over these

88   regions will be discussed to investigate the possible regional discrepancies in surface and free

89   tropospheric O_3 changes associated with different local pollution levels. Our conclusions

90   follow in Section 4.

91

2. Data and Methods

2.1 OMI and surface O_3 measurements

94   The OMI O_3 profile retrieval product (PROFOZ v0.9.3, level 2, Liu et al., 2010; Huang

95   et al., 2017) from the Smithsonian Astrophysical Observatory (SAO) was assimilated in this

96   work. The OMI instrument provides global covered measurements with backscattered sunlight

97   in the ultraviolet–visible range from 270 to 500 nm (UV1: 270–310 nm; UV2: 310–365 nm;

98   visible: 350–500 nm) with a spatial resolution of 13 × 24 km (nadir view). Following Huang et

99   al. (2017), the following filters are applied: 1) nearly clear-sky scenes with effective cloud

100 fraction < 0.3; 2) solar zenith angles (SZA) < 75°; and 3) fitting root mean square (RMS, ratio

101 of fitting residuals to assumed measurement error) < 2.0. Starting in 2009, anomalies were

102 found in OMI data and diagnosed as attenuated measured radiances in certain cross-track

103 positions. This instrument degradation has been referred to as the "row anomaly". To enhance

104 the quality and stability of data, only across-track positions between 4-11 (within 30 positions

105 in the UV1 channels) are used in our analysis. This treatment is similar to the production of

106 row-isolated data by using across-track positions between 3-18 (within 60 positions in the UV2

107 channels) in the OMI/MLS O_3 data (Ziemke et al., 2019; Wang et al., 2022).

108 We use in situ hourly surface O_3 measurements from the US AQS and European

109 Environment Agency AirBase networks. The AQS and AirBase networks collect ambient air

110 pollution data from monitoring stations located in urban, suburban, and rural areas. To ensure

111 the long-term stability of the observation record, we only considered stations with at least 14

112 years of observation records in 2005-2020. Observations provided by the AQS and AirBase

113 stations have been widely used in previous studies to investigate the sources and variabilities

114 of surface O_3 pollution (Shen et al., 2015; Boleti et al., 2020; He et al., 2022).

115 **2.2 Single O_3 tracer simulation and assimilation system**

116 The GEOS-Chem chemical transport model (http://www.geos-chem.org, version 12-8-1)

117 is driven by assimilated meteorological data of MERRA-2. The GEOS-Chem full chemistry

118 simulation includes fully coupled O_3-NO_x-VOC-halogen-aerosol chemistry. Our analysis is

119 conducted at a horizontal resolution of nested $0.5°\times0.625°$ over the US and Europe with

120 chemical boundary conditions archived every 3 hours from global simulations with $4°\times5°$

121 resolution. Emissions are computed by the Harvard-NASA Emission Component (HEMCO).

122 Global default anthropogenic emissions are from the CEDS (Community Emissions Data

123 System) (Hoesly et al., 2018). Regional emissions are replaced by MEIC (Multiresolution

124 Emission Inventory for China) in China, MIX in other regions of Asia (Li et al., 2017) and

125 NEI2011 in the US. Open fire emissions are from the Global Fire Emissions Database (GFED4)

126 (van der Werf et al., 2010).

127 Following Jiang et al. (2022), the total anthropogenic NO_x and VOC emissions in the

128 GEOS-Chem model are scaled with the corresponding bottom-up inventories (MEIC for China,

129 NEI2014 for the US and ECLIPSE for Europe) so that the modeled surface nitrogen dioxide

130 (NO_2) and VOC concentrations in the a priori simulations are identical to Jiang et al. (2022) in

131 2005-2018. The total anthropogenic NO_x and VOC emissions in 2019-2020 in China, the US

132   and Europe are further scaled based on linear projections. The total anthropogenic NO_x

133   emissions in the a priori simulations declined by 53% (US) and 50% (Europe) in 2005-2020.

134   The total anthropogenic VOC emissions in the a priori simulations declined by 19% (US) and

135   33% (Europe) in 2005-2020. We refer the reader to Jiang et al. (2022) for the details of the

136   model configuration and performance, particularly the modeled trends of surface and

137   tropospheric column NO_2 in 2005-2018.

138   A new single O_3 tracer mode (tagged-O_3) was developed in the companion paper (Zhu et

139   al., 2023) by reading the archived production (PO3) and loss (LO3) of O_3 provided by the full

140   chemistry simulation. The major advantage of the single O_3 tracer mode is dramatic reductions

141   in computational costs by approximately 91-94% (Zhu et al., 2023). Fig. S1 and Fig. S2 (see

142   the SI) show the annual and seasonal averages of surface maximum daily 8-

143   hour average (MDA8) O_3 over the US and Europe in 2005-2020 from the full chemistry and

144   single O_3 tracer simulations (i.e., the a priori simulations in this work), respectively. We find

145   good spatial (Fig. S1 and Fig. S2) as well as temporal (Fig. S3, see the SI) consistencies in

146   surface MDA8 O_3 between full chemistry and single O_3 tracer simulations over the US and

147   Europe in 2005-2020. The computation costs (hours of wall time for one year simulation) are

148   160.7 and 9.4 hours within the nested US domain (0.5°×0.625°) and 103.4 and 6 hours within

149   the nested Europe domain (0.5°×0.625°) by full chemistry and single O_3 tracer mode,

150   respectively.

151   The low computational costs of the single O_3 tracer mode allow us to perform O_3

152   assimilations more efficiently. The sequential KF was conducted to assimilate AQS, AirBase

153   and OMI O_3 observations to produce the a posteriori O_3 concentrations. As a brief description

154   of the assimilation algorithm, the forward model (**M**) predicts the O_3 concentration (x_{at}) at

155   time t:

156                    $$x_{at} = M_t x_{t-1} \quad (Eq. 1)$$

157   The optimized O_3 concentrations can be expressed as:

158    $$x_t = x_{at} + G_t(y_t - K_t x_{at}) \quad (Eq.\,2)$$

159   where y_t is the observation (i.e., OMI or surface O_3 observations) and K_t represents the

160   operation operator that projects O_3 concentrations from the model space to the observation

161   space. G_t is the KF gain matrix, which can be described as:

162    $$G_t = S_{at}K_t^T(K_t S_{at} K_t^T + S_\epsilon)^{-1} \quad (Eq.\,3)$$

163   where S_{at} and S_ϵ are the model and observation covariances, respectively. The modeled

164   tropospheric O_3 profiles in the OMI-based assimilation processes are convolved by using the

165   OMI retrieval averaging kernels. The mixing of O_3 precursors in the planetary boundary layer

166   is considered with a simplified planetary boundary layer parameterization in surface

167   observation-based assimilations. We refer the reader to the companion paper (Zhu et al., 2023)

168   for more details about the development and performance of the single O_3 tracer assimilation

169   system by assimilating satellite and surface O_3 observations.

170

171   **3. Results and Discussion**

172   **3.1 Surface O_3 by assimilating surface O_3 observations**

173   Fig. 2a-e and Fig. 3a-e show the annual and seasonal averages of surface MDA8 O_3

174   observations from US AQS and European AirBase stations in 2005-2020. Fig. 2k-o and Fig.

175   3k-o further show the annual and seasonal averages of the a posteriori O_3 concentrations by

176   assimilating AQS or AirBase O_3 observations. As shown in Fig. 4 and Fig. 5, the assimilated

177   O_3 concentrations (blue lines) show good agreements with surface O_3 observations (red lines):

178   the mean surface MDA8 O_3 in 2005-2020 are 41.4, 39.5 and 39.5 ppb (US), 40.0, 37.7 and

179   38.2 ppb (Great Lakes), 38.1, 36.4 and 37.4 ppb (Northeast US), 41.6, 41.2 and 41.0 ppb (West

180   Coast), 42.2, 40.4 and 39.7 ppb (Middle US), 44.4, 40.3 and 39.9 ppb (Southeast US) in the a

181   priori simulations, a posteriori simulations and AQS observations, respectively; the mean

182　surface MDA8 O_3 in 2005-2020 are 35.3, 32.0 and 31.6 ppb (Europe), 29.9, 26.0 and 24.4 ppb

183　(Britain), 30.5, 28.2 and 28.0 ppb (Central EU), 35.9, 32.5 and 32.3 ppb (Western EU), 40.3,

184　35.2 and 34.2 ppb (Iberian Peninsula), 41.8, 35.3 and 34.0 ppb (Apennine Peninsula) in the a

185　priori simulations, a posteriori simulations and AirBase observations, respectively.

186　　　Similar to China, we find overestimated summertime surface O_3 concentrations in the a

187　priori simulations over the US and Europe (Fig. 4 and Fig. 5). However, in contrast to the

188　underestimated O_3 declines in June-July in China (Zhu et al., 2023), the overestimated

189　summertime O_3 over the US and Europe are caused by overestimated increases in surface O_3

190　in July-August, which have led to surface MDA8 O_3 maximum in July-August in the

191　simulations. In contrast, assimilations suggest that surface O_3 is broadly maximum in April

192　over the US and Europe (Fig. 4 and Fig. 5), although O_3 seasonality varies over different

193　regions. We find good agreements in surface O_3 concentrations between a priori and a

194　posteriori simulations over the US in seasons outside of summer (Fig. 2p-t), in contrast to the

195　large differences between a priori and a posteriori simulations over Europe (Fig. 3p-t in this

196　work) and China (Zhu et al., 2023). The inaccurate surface O_3 concentrations over three

197　continents reveal possible uncertainties in model simulations, particularly the contributions

198　from natural and anthropogenic processes; for example, the higher temperature and solar

199　radiation can lead to high O_3 concentrations in August, whereas the transport of O_3 and its

200　precursors can lead to high O_3 concentrations in April (Parrish et al., 2013).

201　　　Furthermore, our analysis exhibits high surface MDA8 O_3 concentrations over the West

202　Coast (41.2 ppb) in the US. Except for the West Coast, the assimilated surface MDA8 O_3

203　concentrations are lower over areas with higher anthropogenic NO_x emissions over the US and

204　Europe. For example, 37.7 and 36.4 ppb in the Great Lakes and Northeast US, respectively, in

205　contrast to 40.4 and 40.3 ppb in the Middle US and Southeast US, respectively; and 26.0 and

206　28.2 ppb in the Britain and Central EU, respectively, in contrast to 32.5, 35.2 and 35.3 ppb in

207 the Western EU, Iberian Peninsula and Apennine Peninsula, respectively. The inverse

208 relationships between surface O_3 concentrations and local anthropogenic NO_x emissions

209 indicate the important impacts of natural sources and meteorological conditions on surface O_3

210 pollution over the US and Europe because of continuous declines in anthropogenic emissions

211 in the past decades. This is the opposite of the higher O_3 concentrations in areas with higher

212 local anthropogenic NO_x emissions in China (Zhu et al., 2023), where surface O_3 pollution is

213 strongly affected by anthropogenic emissions.

3.2 Limited changes in surface O_3 concentrations

215 Following Jiang et al. (2022), the anthropogenic NO_x and VOC emissions over the US

216 in 2005-2020 declined by 53% (-5.1% yr^{-1}) and 19% (-1.4% yr^{-1}) in our a priori simulations,

217 which is accompanied by slight decreasing trends in surface MDA8 O_3 in the a priori

218 simulations (Table 1.1): -0.29 (spring), -0.45 (summer), -0.07 (autumn) and 0.05 (winter) ppb

219 yr^{-1}; and the relative trends are -0.7 (spring), -0.9 (summer), -0.2 (autumn) and 0.2 (winter) %

220 yr^{-1}. Similarly, the anthropogenic NO_x and VOC emissions over Europe in 2005-2020 declined

221 by 50% (-4.4% yr^{-1}) and 33% (-2.7% yr^{-1}) in our a priori simulations, which is accompanied

222 by slightly increasing trends of surface MDA8 O_3 in the a priori simulations (Table 2.1): -0.07

223 (spring), -0.07 (summer), 0.07 (autumn) and 0.24 (winter) ppb yr^{-1}; and the relative trends are

224 -0.2 (spring), -0.2 (summer), 0.2 (autumn) and 1.0 (winter) % yr^{-1}. It is surprising to see the

225 limited changes in surface O_3 concentrations in the simulations accompanied by dramatic

226 declines in anthropogenic emissions.

227 We thus further investigate the changes in surface O_3 by assimilating surface O_3

228 observations. As shown in Table 1.1 and Fig. 6k-o, our assimilations suggest -0.27 (spring), -

229 0.46 (summer), -0.12 (autumn) and 0.11 (winter) ppb yr^{-1} changes in surface MDA8 O_3 over

230 the US in 2005-2020, and the relative changes are -0.6 (spring), -1.0 (summer), -0.3 (autumn)

231 and 0.4 (winter) % yr^{-1}. Similarly, as shown in Table 2.1 and Fig. 7k-o, our assimilations

232 suggest -0.04 (spring), -0.03 (summer), 0.09 (autumn) and 0.19 (winter) ppb yr^{-1} changes in

233 surface MDA8 O_3 over Europe in 2005-2020, and the relative changes are -0.1 (spring), -0.1

234 (summer), 0.3 (autumn) and 0.9 (winter) % yr^{-1}. In contrast to the underestimated increasing

235 trends in surface O_3 concentrations in the a priori simulations in China (Zhu et al., 2023), we

236 find broadly consistent trends between simulations and assimilations over the US and Europe,

237 which confirms the limited changes in surface O_3 concentrations over the US and Europe.

238   The changes in surface O_3 concentrations have marked regional and seasonal

239 discrepancies. As shown in Tables S1-S5 (see the SI), our assimilations demonstrate stronger

240 increasing trends in surface O_3 concentrations in 2005-2020 in the winter (0.39 ppb yr^{-1} or 1.5%

241 yr^{-1}) over the Great Lakes, in the winter (0.36 ppb yr^{-1} or 1.4% yr^{-1}) over the Northeast US, in

242 the autumn (0.34 ppb yr^{-1} or 0.8% yr^{-1}) and winter (0.29 ppb yr^{-1} or 1.0% yr^{-1}) over the West

243 Coast, as well as decreasing trends in surface O_3 concentrations in 2005-2020 in the summer

244 over the Great Lakes (-0.51 ppb yr^{-1} or -1.0% yr^{-1}), Northeast US (-0.52 ppb yr^{-1} or -1.1% yr^{-1}),

245 Middle US (-0.61 ppb yr^{-1} or -1.3% yr^{-1}) and Southeast US (-0.87 ppb yr^{-1} or -1.9% yr^{-1}). The

246 areas with higher anthropogenic NO_x emissions such as the Great Lakes and Northeast US

247 demonstrate lower surface O_3 concentrations and are accompanied by stronger increasing

248 trends in the winter and weaker decreasing trends in the summer.

249   Tables S6-S10 (see the SI) further show the details of tropospheric O_3 changes in Europe.

250 Our assimilations demonstrate stronger increasing trends in surface O_3 concentrations in 2005-

251 2020 in the winter over Britain (0.28 ppb yr^{-1} or 1.5% yr^{-1}), Central EU (0.26 ppb yr^{-1} or 1.5%

252 yr^{-1}), Western EU (0.25 ppb yr^{-1} or 1.1% yr^{-1}), Iberian Peninsula (0.17 ppb yr^{-1} or 0.6% yr^{-1})

253 and Apennine Peninsula (0.18 ppb yr^{-1} or 0.8% yr^{-1}), as well as decreasing trends in surface O_3

254 concentrations in 2005-2020 in the summer (-0.07 ppb yr^{-1} or -0.2% yr^{-1}) over Britain, in the

255 summer (-0.10 ppb yr^{-1} or -0.2% yr^{-1}) over the Western EU, in the summer (-0.20 ppb yr^{-1} or -

256 0.5% yr^{-1}) over the Iberian Peninsula and in the spring (-0.09 ppb yr^{-1} or -0.2% yr^{-1}) over the

257   Apennine Peninsula. Similar to the US, areas with higher anthropogenic NO_x emissions such

258   as Britain and Central EU demonstrate lower surface O_3 concentrations and are accompanied

259   by stronger increasing trends in the winter and weaker decreasing trends in the summer.

260   Furthermore, Zhu et al. (2023) demonstrated a large discrepancy in the trends in

261   assimilated surface O_3 between urban (i.e., areas with air quality stations) and regional

262   backgrounds in China in 2015-2020: 3.0% yr^{-1} (sampled at air quality stations) and 1.3% yr^{-1}

263   (land average). In contrast, we did not find a comparable discrepancy over the US and Europe:

264   the trends of assimilated surface O_3 are -0.4% yr^{-1} (Table 1.1, sampled at AQS O_3 observations)

265   and -0.4% yr^{-1} (Table 1.2, land average) over the US and -0.2% yr^{-1} (Table 2.1, sampled at

266   AirBase O_3 observations) and 0.0% yr^{-1} (Table 2.2, land average) over Europe. The difference

267   between China and the US/Europe suggests more consistent changes in surface O_3 between

268   urban and regional background areas in the US and Europe. This implies possible larger relative

269   contributions of regional background O_3 to surface O_3 observations in the US and Europe,

270   which could be associated with the limited changes in surface O_3 concentrations in 2005-2020

271   because regional background O_3 is less sensitive to changes in anthropogenic NO_x and VOC

272   emissions.

273   **3.3 Tropospheric O_3 columns by assimilating OMI O_3 observations**

274   Fig. S4a-e and Fig. S5a-e (see the SI) show the annual and seasonal averages of

275   tropospheric OMI O_3 columns in 2005-2020 over the US and Europe, respectively. Fig. S4k-o

276   and Fig. S5k-o further show the annual and seasonal averages of the a posteriori tropospheric

277   O_3 columns by assimilating OMI O_3 observations. The assimilated tropospheric O_3 columns

278   show good agreement with OMI O_3 observations: the mean tropospheric O_3 columns over the

279   US in 2005-2020 (Table 1.3) are 35.5 DU in the a priori simulations, and 37.0 and 36.8 DU in

280   the a posteriori simulations and OMI observations, respectively; the mean tropospheric O_3

281   columns over Europe in 2005-2020 (Table 2.3) are 32.8 DU in the a priori simulations, and

282   35.3 and 36.4 DU in the a posteriori simulations and OMI observations, respectively. However,

283   there are small deviations in the trends between assimilations and OMI observations. As shown

284   in Fig. S6-S7 (see the SI), the trends of tropospheric O_3 columns over the US in 2005-2020

285   (Table 1.3) are -0.11 DU yr^{-1} in the a priori simulations, and -0.16 and -0.01 DU yr^{-1} in the a

286   posteriori simulations and OMI observations, respectively; the trends of tropospheric O_3

287   columns over Europe in 2005-2020 (Table 2.3) are -0.09 DU yr^{-1} in the a priori simulations,

288   and -0.25 and -0.15 DU yr^{-1} in the a posteriori simulations and OMI observations, respectively.

289   These deviations are associated with the adjustments to regional O_3 boundary conditions in the

290   nested assimilations by assimilating global OMI O_3 observations, reflecting the different

291   changes in OMI O_3 between US/Europe continents and global backgrounds. For example, the

292   mean tropospheric O_3 columns over the US in 2005 are 36.5 DU in OMI observations, and 35.9

293   and 37.5 DU in the assimilations by reading a priori and adjusted O_3 boundary conditions,

294   respectively; the mean tropospheric O_3 columns over Europe in 2005 are 37.5 DU in OMI

295   observations, and 34.6 and 36.9 DU in the assimilations by reading a priori and adjusted O_3

296   boundary conditions, respectively.

297   The annual averages of surface MDA8 O_3 in the a priori simulation and assimilations are

298   35.3 and 32.0 ppb with a relative difference of 10% over Europe (Table 2.1); 41.4 and 39.5 ppb

299   with a relative difference of 5% over the US (Table 1.1); and 42.9 and 41.8 ppb with a relative

300   difference of 3% over China (Zhu et al., 2023). In addition, the annual averages of tropospheric

301   O_3 columns in the a priori simulation and assimilations are 32.8 and 35.3 DU with a relative

302   difference of -7% over Europe (Table 2.3); 35.5 and 37.0 DU with a relative difference of -4%

303   over the US (Table 1.3); and 37.1 and 37.9 DU with a relative difference of -2% over China

304   (Zhu et al., 2023). It seems that the GEOS-Chem model has a better performance in regional

305   averages of surface and free tropospheric O_3 concentrations in China and the US than in

306   Europe.

307   The output O_3 profiles from a priori and a posteriori simulations are convolved with OMI

308   averaging kernels in Fig. S4-S7. However, the convolution of OMI O_3 averaging kernels on

309   the output O_3 profiles can affect the weights of the derived tropospheric columns to O_3 at

310   different vertical levels and thus may not accurately represent the actual tropospheric O_3

311   columns. Fig. 8 and Fig. 9 further show tropospheric O_3 columns from a priori and a posteriori

312   simulations, in which the output O_3 profiles are not convolved with OMI averaging kernels.

313   The assimilated tropospheric O_3 columns are 35.6 and 38.7 DU (US), 36.8 and 40.2 DU (Great

314   Lakes), 36.8 and 40.3 DU (Northeast US), 38.1 and 41.9 DU (West Coast), 38.9 and 41.5 DU

315   (Middle US), 43.5 and 45.8 DU (Southeast US) in 2005-2020 by assimilating AQS and OMI

316   O_3 observations, respectively; the assimilated tropospheric O_3 columns are 31.5 and 35.9 DU

317   (Europe), 29.7 and 34.7 DU (Britain), 30.4 and 34.9 DU (Central EU), 31.8 and 36.4 DU

318   (Western EU), 33.6 and 38.1 DU (Iberian Peninsula), 34.0 and 38.2 DU (Apennine Peninsula)

319   in 2005-2020 by assimilating AirBase and OMI O_3 observations, respectively. We find that

320   tropospheric O_3 columns obtained by assimilating surface O_3 observations are lower than those

321   obtained by assimilating OMI O_3 observations. Similar to surface O_3 concentrations,

322   tropospheric O_3 columns are lower over areas with higher anthropogenic NO_x emissions over

323   the US and Europe such as the Great Lakes, Northeast US, Britain and Central EU. This is

324   opposite to the higher tropospheric O_3 columns over areas with higher local anthropogenic NO_x

325   emissions in China (Zhu et al., 2023).

326   In contrast to the surface MDA8 O_3 maximum in April in the observations (Fig. 4 and

327   Fig. 5), the assimilated tropospheric O_3 columns are broadly maximum in July-August over the

328   US and Europe (Fig. 10 and Fig. 11). The free tropospheric O_3 maximum in the summer has

329   been reported in previous studies. For example, Wespes et al. (2018) demonstrated a free

330   tropospheric O_3 maximum in summer over Europe by using Infrared Atmospheric Sounding

331   Interferometer (IASI) observations; Petetin et al. (2016) exhibited a free tropospheric O_3

332 maximum in summer over Europe by using MOZAIC aircraft measurements. We find good

333 agreement in the seasonality of free tropospheric O_3 between simulations and assimilations in

334 contrast to the inaccurate simulation of the seasonality of surface O_3 concentrations in the

335 simulations. More studies are needed in the future to explore the sources of this difference in

336 model performance.

337   Furthermore, Fig. S8-S9 (see the SI) demonstrate the O_3 vertical profiles in 2005-2009,

338 2010-2014 and 2015-2020, respectively. The assimilation of surface O_3 observations leads to

339 decreases in O_3 concentrations in the lower troposphere but has small impacts on free

340 tropospheric O_3. In contrast, the assimilation of OMI O_3 observations leads to dramatic

341 enhancements in O_3 concentrations in the middle and upper troposphere without noticeable

342 differences between areas with high and low local anthropogenic NO_x emissions. The

343 enhancement in free tropospheric O_3 by assimilating OMI O_3 observations declined gradually

344 from 2005-2009 to 2015-2020. The adjustment in free tropospheric O_3 by assimilating OMI O_3

345 observations in 2015-2020 is larger but comparable with the adjustment in 2015-2020 in China

346 (Zhu et al., 2023).

3.4 Large decreases in tropospheric O_3 columns

348   Fig 12 and Fig. 13 show the trends in tropospheric O_3 columns in 2005-2020 from a priori

349 simulations and a posteriori simulations by assimilating surface and OMI O_3 observations. The

350 trends of tropospheric O_3 columns in 2005-2020 are -0.07, -0.07 and -0.29 DU yr^{-1} (US), -0.03,

351 -0.03 and -0.29 DU yr^{-1} (Great Lakes), -0.02, -0.02 and -0.31 DU yr^{-1} (Northeast US), -0.02, -

352 0.01 and -0.26 DU yr^{-1} (West Coast), -0.08, -0.07 and -0.24 DU yr^{-1} (Middle US), -0.19, -0.18

353 and -0.28 DU yr^{-1} (Southeast US) in the a priori simulations and a posteriori simulations by

354 assimilating AQS and OMI O_3 observations, respectively; and are 0.03, 0.03 and -0.36 DU yr^{-}

355 ^{1} (Europe), 0.00, 0.00 and -0.49 DU yr^{-1} (Britain), 0.04, 0.04 and -0.38 DU yr^{-1} (Central EU),

356 0.02, 0.03 and -0.36 DU yr^{-1} (Western EU), 0.02, 0.02 and -0.30 DU yr^{-1} (Iberian Peninsula), -

357 0.04, 0.04 and -0.26 DU yr^{-1} (Apennine Peninsula) in the a priori simulations and a posteriori

358 simulations by assimilating AirBase and OMI O$_3$ observations, respectively. Our analysis thus

359 exhibits dramatically lower decreasing trends in tropospheric O$_3$ columns in the a priori

360 simulations and assimilations by assimilating surface O$_3$ observations with respect to OMI-

361 based assimilations.

362 The limited changes in surface O$_3$ concentrations in the a priori simulations and

363 assimilations by assimilating surface O$_3$ observations indicate limited influences of declines in

364 local anthropogenic emissions on surface O$_3$ concentrations in the US and Europe in 2005-

365 2020. We can thus expect insignificant influences of the vertical transport of surface O$_3$ on the

366 changes in free tropospheric O$_3$ over the US and Europe in 2005-2020, as illustrated by the flat

367 trends in tropospheric O$_3$ columns in the a priori simulations and assimilations by assimilating

368 surface O$_3$ observations (Fig. 10 and Fig. 11), as well as the small impacts of assimilation of

369 surface O$_3$ observations on free tropospheric O$_3$ (Fig. S8-S9). However, as indicated by Jiang

370 et al. (2022), tropospheric OMI NO$_2$ columns declined by 36% and 23% in 2005-2018 over the

371 US and Europe, respectively. Are the large decreases in tropospheric O$_3$ columns by

372 assimilating OMI O$_3$ observations, i.e., 12.0% (US) and 15.0% (Europe) in 2005-2020, caused

373 by the declines in free tropospheric NO$_2$?

374 As indicated by Jiang et al. (2022), tropospheric OMI NO$_2$ columns declined by -7.0%

375 yr^{-1} (US) and -4.2% yr^{-1} (Europe) in 2005-2010, which was followed by a dramatic slowdown

376 in the decreasing trends, i.e., -1.7% yr^{-1} (US) and -1.2% yr^{-1} (Europe) in 2010-2018. However,

377 as shown in Table 1.4, tropospheric O$_3$ columns obtained by assimilating OMI O$_3$ observations

378 declined by -0.3, -2.3 and -0.5% yr^{-1} over the US in 2005-2009, 2010-2014 and 2015-2020,

379 respectively. Similarly, tropospheric O$_3$ columns obtained by assimilating OMI O$_3$

380 observations declined by -1.0, -2.3 and -0.8% yr^{-1} over Europe (Table 2.4) in 2005-2009, 2010-

381 2014 and 2015-2020, respectively. The OMI-based declines in tropospheric O$_3$ columns over

382   the US and Europe mainly occurred in the period with slowed decreases in free tropospheric

383   NO$_2$ after 2010; in contrast, the dramatic declines in tropospheric NO$_2$ columns before 2010

384   were accompanied by limited changes in free tropospheric O$_3$. It is thus difficult to conclude

385   that the large decreases in tropospheric O$_3$ columns over the US and Europe in 2010-2014 are

386   dominated by declines in local anthropogenic NO$_x$ emissions.

387   We note our OMI-based analysis could be affected by the row anomaly issue, although

388   the usage of "row-isolated" data by using across-track positions between 4-11 in this work is

389   expected to reduce the impacts of row anomaly. As shown by Huang et al. (2017), the row

390   anomaly can lead to discontinuity in the trends in OMI O$_3$ observations in 2009. However, the

391   large decreases in tropospheric O$_3$ columns over the US and Europe mainly occurred after

392   2010. Consequently, we assume a limited influence of row anomaly on our conclusion.

393   Furthermore, OMI is sensitive to O$_3$ concentrations in the free troposphere; OMI-based

394   assimilations are driven by adjusted regional O$_3$ boundary conditions provided by global OMI

395   O$_3$ assimilations and can reflect optimized adjustments in both local and global background O$_3$

396   concentrations. In contrast, surface observations are sensitive to local O$_3$ concentrations;

397   surface observation-based assimilations are driven by the a priori O$_3$ boundary conditions,

398   which thus reflects the optimized adjustments in local contributions and is also affected by

399   lacking optimization on the impacts of O$_3$ precursors due to the single O$_3$ tracer simulations.

400   These factors contributed to the difference in the trends of tropospheric O$_3$ columns by

401   assimilating surface and satellite observations. Assimilations of both surface and satellite

402   observations, as shown in this work, are expected to provide more information to better

403   characterization of the changes and uncertainties in free tropospheric O$_3$.

404   **4. Conclusion**

405   As a companion paper of Zhu et al. (2023) which focuses on tropospheric O$_3$ change in

406   China in 2015-2020, this paper investigates the changes in surface and free tropospheric O$_3$

407   over the US and Europe in 2005-2020 by assimilating OMI, AQS and AirBase O_3 observations.

408   The assimilated O_3 concentrations demonstrate good agreement with O_3 observations: surface

409   O_3 concentrations are 41.4, 39.5 and 39.5 ppb (US) and 35.3, 32.0 and 31.6 ppb (Europe) in

410   the a priori and a posteriori simulations and AQS and AirBase O_3 observations, respectively;

411   and tropospheric O_3 columns are 35.5, 37.0 and 36.8 DU (US) and 32.8, 35.3 and 36.4 DU

412   (Europe) in the a priori and a posteriori simulations (convolved with OMI retrieval averaging

413   kernels) and OMI O_3 observations, respectively. The modeled surface O_3 by GEOS-Chem is

414   overestimated in the summer, which results in a surface O_3 maximum in July-August in the

415   simulations in contrast to April in the observations; in contrast, GEOS-Chem demonstrates

416   good performance in the simulation of seasonality in free tropospheric O_3, which is maximum

417   in July-August. In addition, we find lower surface O_3 concentrations over areas with higher

418   anthropogenic NO_x emissions in the US and Europe. This is the opposite of the higher O_3

419   concentrations in areas with higher local anthropogenic NO_x emissions in China (Zhu et al.,

420   2023).

421   Our analysis exhibits a noticeable decrease in surface O_3 concentrations over the US in

422   the summer by 15% in 2005-2020. However, accompanied by approximately 50% reductions

423   in NO_x emissions, changes in surface O_3 concentrations are limited in Europe and other seasons

424   in the US: the annual surface MDA8 O_3 decreased by -6% over the US and increased by 1.5%

425   over Europe in 2005-2020, and the decreases in surface O_3 concentrations are weaker over

426   areas with higher local anthropogenic NO_x emissions. Furthermore, the surface observation-

427   based assimilations suggest insignificant changes in tropospheric O_3 columns: -3.0% (US) and

428   1.5% (Europe) in 2005-2020. While the OMI-based assimilations exhibit large decreases in

429   tropospheric O_3 columns, i.e., -12.0% (US) and -15.0% (Europe) in 2005-2020, the decreases

430   in tropospheric O_3 columns mainly occurred in 2010-2014, corresponding to reported slowed

431   declines in free tropospheric NO_2 since 2010 (Jiang et al., 2022). Despite the dramatic declines

432   in tropospheric NO_2, particularly, declines in tropospheric NO_2 columns in 2005-2010, our

433   analysis suggests limited impacts of local emission declines on changes in tropospheric O_3 over

434   the US and Europe because the rapid decline in tropospheric NO_2 columns in 2005-2010

435   corresponds to relatively flat trends in tropospheric O_3. More efforts are suggested to evaluate

436   the contributions of natural sources and transport to tropospheric O_3 changes, which is critical

437   for making more effective policies to reduce O_3 pollution.

438

439   **Code and data availability:** The AQS and AirBase surface O_3 data can be downloaded from

440   https://www.eea.europa.eu/data-and-maps/data/aqereporting-8 and

441   https://aqs.epa.gov/aqsweb/airdata/download_files.html#Row. The OMI PROFOZ product

442   can be acquired at

443   https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L2/OMPROFOZ/. The GEOS-

444   Chem model (version 12.8.1) can be downloaded from http://wiki.seas.harvard.edu/geos-

445   chem/index.php/GEOS-Chem_12#12.8.1. The KPP module for tagged-O_3 simulations can be

446   downloaded from https://doi.org/10.5281/zenodo.7545944.

447

448   **Competing interests**: The contact author has declared that neither they nor their co-authors

449   have any competing interests.

450

Table and Figures

Table 1. Averages (with units ppb or DU) and trends (with units ppb yr^{-1} or DU yr^{-1}) of surface and tropospheric column O_3 concentrations in 2005-2020 over the US from observations (AQS and OMI) and a priori and a posteriori (KF) simulations. T1.1): the modeled surface O_3 is sampled at the locations and times of AQS surface O_3 observations; T1.2): the modeled surface O_3 is averaged over the US (land only); T1.3): the output O_3 profiles from the a priori and a posteriori simulations are convolved with OMI O_3 averaging kernels; T1.4): the output O_3 profiles are NOT convolved with OMI O_3 averaging kernels. The uncertainties in the averages are calculated using the bootstrapping method. The trends and uncertainties in the trends are calculated using the linear fitting of averages by using the least squares method (see details in the SI).

Table 2. Averages (with units ppb or DU) and trends (with units ppb yr^{-1} or DU yr^{-1}) of surface and tropospheric column O_3 concentrations in 2005-2020 over Europe from observations (AirBase and OMI) and a priori and a posteriori (KF) simulations. T2.1): the modeled surface O_3 are sampled at the locations and times of AirBase surface O_3 observations; T2.2): the modeled surface O_3 are averaged over Europe (land only); T2.3): the output O_3 profiles from the a priori and a posteriori simulations are convolved with OMI O_3 averaging kernels; T2.4): the output O_3 profiles are NOT convolved with OMI O_3 averaging kernels.

Fig. 1. (a) Anthropogenic NO_x emissions over the US in 2015; (b) Region definitions for Great Lakes (#1), Northeast US (#2), West Coast (#3), Middle US (#4) and Southeast US (#5). Regions #1-3 are defined as highly polluted (HP) regions by excluding grids with low and medium anthropogenic NO_x emissions. (c) Anthropogenic NO_x emissions over Europe in 2015; (d) Region definitions for Britain (#1), Central EU (#2), Western EU (#3), Iberian Peninsula (#4) and Apennine Peninsula (#5). Regions #1 and #2 are defined as highly polluted (HP) regions by excluding grids with low and medium anthropogenic NO_x emissions. The different colors (red, gray and green) represent grids with high (highest 15%), medium (15-50%) and low (lowest 50%) anthropogenic NO_x emissions.

Fig. 2. Surface MDA8 O_3 over the US in 2005-2020 (annual and seasonal averages) from (a-e) AQS stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori

simulation by assimilating AQS O_3 observations. (p-t) Bias in the a priori simulations calculated by a priori minus a posteriori O_3 concentrations.

Fig. 3. Surface MDA8 O_3 over Europe in 2005-2020 (annual and seasonal averages) from (a-e) AirBase stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AirBase O_3 observations. (p-t) Bias in the a priori simulations calculated by a priori minus a posteriori O_3 concentrations.

Fig. 4. (a-f) Daily averages of surface MDA8 O_3 over the US in 2005-2020 from AQS stations (red) and GEOS-Chem a priori (black) and a posteriori (blue) simulations by assimilating AQS O_3 observations. (g-l) Monthly averages of MDA8 O_3. The dashed lines in panels g-l are annual averages.

Fig. 5. (a-f) Daily averages of surface MDA8 O_3 over Europe in 2005-2020 from AirBase stations (red) and GEOS-Chem a priori (black) and a posteriori (blue) simulations by assimilating AirBase O_3 observations. (g-l) Monthly averages of MDA8 O_3. The dashed lines in panels g-l are annual averages.

Fig. 6. Trends of surface MDA8 O_3 over the US in 2005-2020 (annual and seasonal averages) from (a-e) AQS stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AQS O_3 observations.

Fig. 7. Trends of surface MDA8 O_3 over Europe in 2005-2020 (annual and seasonal averages) from (a-e) AirBase stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AirBase O_3 observations.

Fig. 8. Tropospheric O_3 columns over the US in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AQS surface O_3 observations; (k-o) Assimilations of OMI O_3 observations. (p-t) Difference in tropospheric O_3 columns calculated by OMI-based assimilations minus surface observation-based assimilations.

Fig. 9. Tropospheric O_3 columns over Europe in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AirBase surface O_3

observations; (k-o) Assimilations of OMI O$_3$ observations. (p-t) Difference in tropospheric O$_3$ columns calculated by OMI-based assimilations minus surface observation-based assimilations.

Fig. 10. (a-f) Daily averages of tropospheric O$_3$ columns over the US in 2005-2020 from GEOS-Chem a priori simulation (black) and a posteriori simulations by assimilating AQS (blue) and OMI (red) O$_3$ observations. (g-l) Monthly averages of tropospheric O$_3$ columns. The dashed lines in panels g-l are annual averages.

Fig. 11. (a-f) Daily averages of tropospheric O$_3$ columns over Europe in 2005-2020 from GEOS-Chem a priori simulation (black) and a posteriori simulations by assimilating AirBase (blue) and OMI (red) O$_3$ observations. (g-l) Monthly averages of tropospheric O$_3$ columns. The dashed lines in panels g-l are annual averages.

Fig. 12. Trends of tropospheric O$_3$ columns over the US in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AQS surface O$_3$ observations; (k-o) Assimilations of OMI O$_3$ observations.

Fig. 13. Trends of tropospheric O$_3$ columns over Europe in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AirBase surface O$_3$ observations; (k-o) Assimilations of OMI O$_3$ observations.

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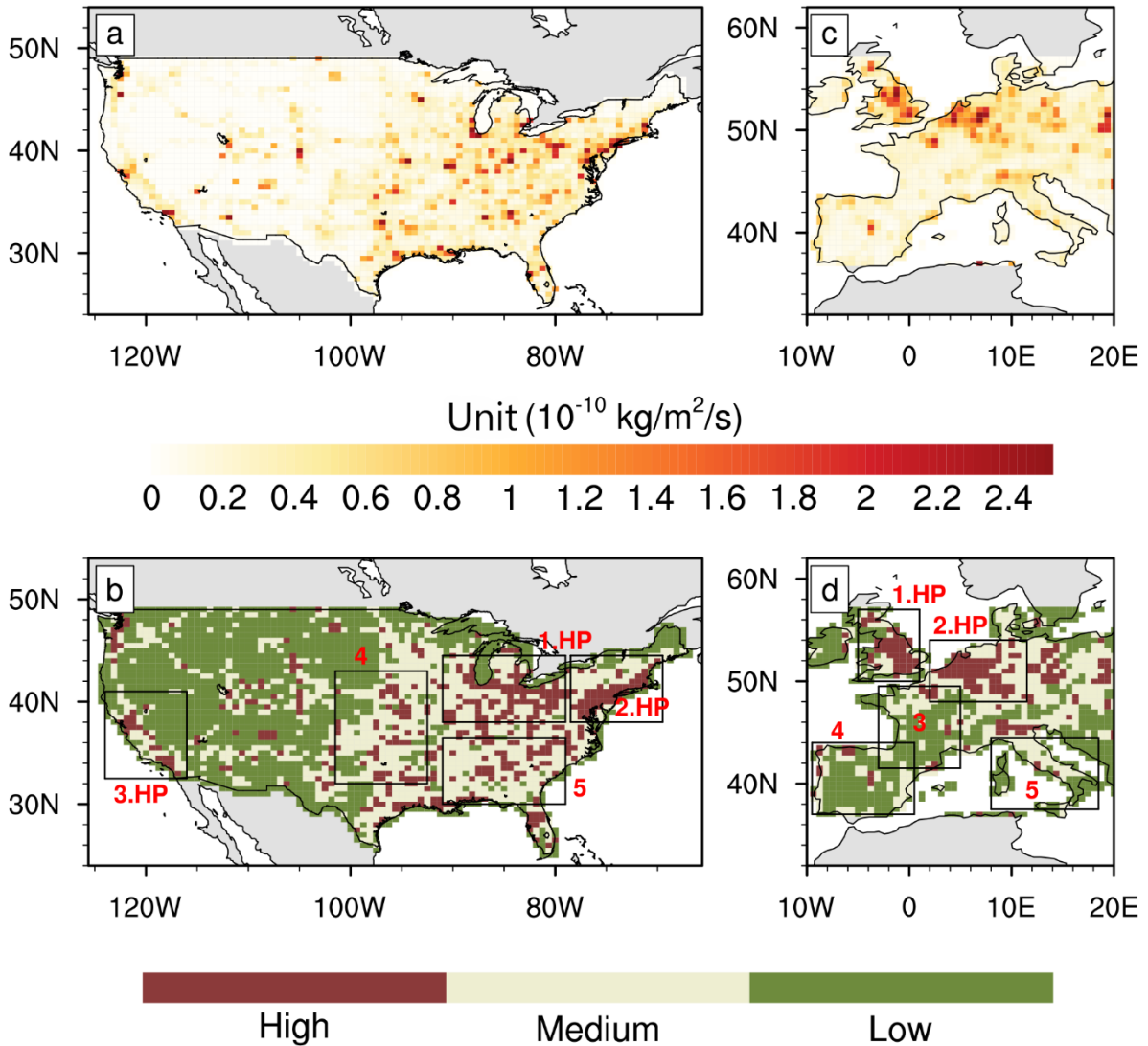667   Chem Phys, 19, 3257-3269, 10.5194/acp-19-3257-2019, 2019.
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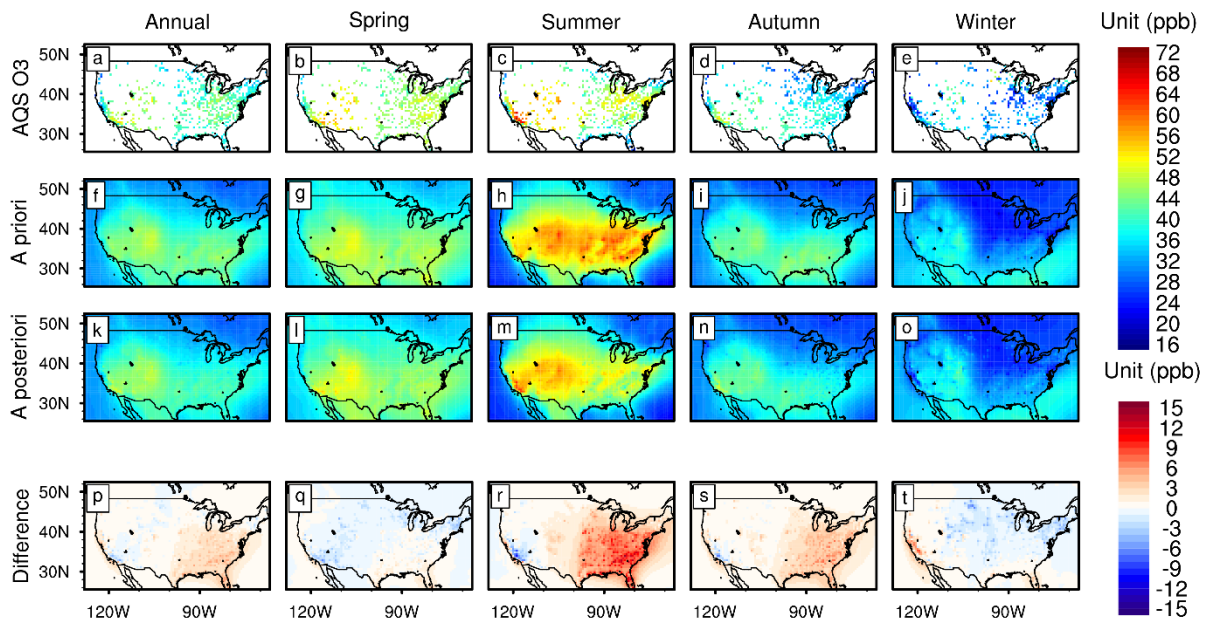| United States			Annual		Spring		Summer		Autumn		Winter	
			Mean	Trend	Mean	Trend	Mean	Trend	Mean	Trend	Mean	Trend
T1.1 surface (sampled)	2005-2020	AQS	39.5±0.2	-0.18±0.04	45.4±0.2	-0.26±0.06	45.2±0.3	-0.49±0.10	36.2±0.2	-0.18±0.09	31.5±0.3	0.14±0.05
		a priori	41.4±0.2	-0.18±0.04	44.2±0.1	-0.29±0.04	51.2±0.3	-0.45±0.11	39.2±0.2	-0.07±0.06	30.9±0.2	0.05±0.05
		KF-AQS	39.5±0.2	-0.17±0.04	44.8±0.1	-0.27±0.05	46.0±0.3	-0.46±0.10	36.3±0.2	-0.12±0.07	31.1±0.2	0.11±0.04
T1.2 surface	2005-2020	a priori	40.3±0.1	-0.17±0.04	43.3±0.1	-0.28±0.05	49.1±0.1	-0.36±0.10	38.1±0.1	-0.10±0.05	30.8±0.1	0.04±0.05
		KF-AQS	39.2±0.1	-0.15±0.03	43.5±0.1	-0.25±0.04	46.1±0.1	-0.34±0.09	36.4±0.1	-0.12±0.05	31.0±0.1	0.07±0.04
T1.3 trop. column (convolved)	2005-2020	OMI	36.8±0.1	-0.01±0.05	38.5±0.1	0.00±0.09	42.1±0.1	0.11±0.08	34.3±0.1	-0.14±0.05	32.0±0.1	-0.03±0.10
		a priori	35.5±0.1	-0.11±0.03	36.9±0.1	-0.14±0.07	41.9±0.1	-0.15±0.06	33.5±0.1	-0.08±0.03	29.8±0.1	-0.06±0.04
		KF-OMI	37.0±0.1	-0.16±0.04	39.4±0.1	-0.21±0.07	43.3±0.1	-0.02±0.06	34.6±0.1	-0.18±0.04	30.7±0.1	-0.21±0.04
T1.4 trop. Column	2005-2020	a priori	35.9±0.1	-0.07±0.04	37.4±0.1	-0.16±0.08	41.2±0.1	-0.17±0.09	33.4±0.1	-0.01±0.06	31.6±0.1	0.02±0.07
		KF-AQS	35.6±0.1	-0.07±0.04	37.4±0.1	-0.15±0.08	40.4±0.1	-0.16±0.09	33.1±0.1	-0.01±0.06	31.6±0.1	0.02±0.07
		KF-OMI	38.7±0.1	-0.29±0.04	41.9±0.1	-0.42±0.09	43.9±0.1	-0.11±0.09	35.6±0.1	-0.26±0.06	33.3±0.1	-0.41±0.10
	2005-2009	KF-AQS	35.7±0.1	-0.25±0.14	37.7±0.2	-0.45±0.39	40.7±0.1	-0.97±0.21	32.9±0.1	-0.12±0.35	31.5±0.2	-0.13±0.33
		KF-OMI	40.1±0.1	-0.13±0.18	43.5±0.1	-0.21±0.40	43.5±0.1	-0.70±0.13	37.1±0.1	-0.18±0.48	36.5±0.1	-0.35±0.32
	2010-2014	KF-AQS	36.1±0.1	-0.51±0.26	38.3±0.1	-0.78±0.62	41.3±0.1	-1.31±0.39	33.3±0.1	-0.17±0.31	31.5±0.1	-0.30±0.65
		KF-OMI	39.1±0.1	-0.89±0.14	43.3±0.1	-1.20±0.56	45.1±0.1	-1.37±0.37	35.4±0.1	-0.41±0.31	31.9±0.1	-0.67±0.63
	2015-2020	KF-AQS	35.1±0.1	0.03±0.11	36.5±0.1	-0.05±0.30	39.6±0.1	0.15±0.35	32.9±0.1	0.04±0.31	31.8±0.1	0.09±0.29
		KF-OMI	37.1±0.1	-0.18±0.13	39.5±0.1	-0.43±0.39	43.2±0.1	-0.02±0.28	34.4±0.1	-0.21±0.25	31.8±0.1	-0.03±0.27

Table. 1. Averages (with units ppb or DU) and trends (with units ppb yr^{-1} or DU yr^{-1}) of surface and tropospheric column O_3 concentrations in 2005-2020 over the US from observations (AQS and OMI) and a priori and a posteriori (KF) simulations. T1.1): the modeled surface O_3 is sampled at the locations and times of AQS surface O_3 observations; T1.2): the modeled surface O_3 is averaged over the US (land only); T1.3): the output O_3 profiles from the a priori and a posteriori simulations are convolved with OMI O_3 averaging kernels; T1.4): the output O_3 profiles are NOT convolved with OMI O_3 averaging kernels. The uncertainties in the averages are calculated using the bootstrapping method. The trends and uncertainties in the trends are calculated using the linear fitting of averages by using the least squares method (see details in the SI).

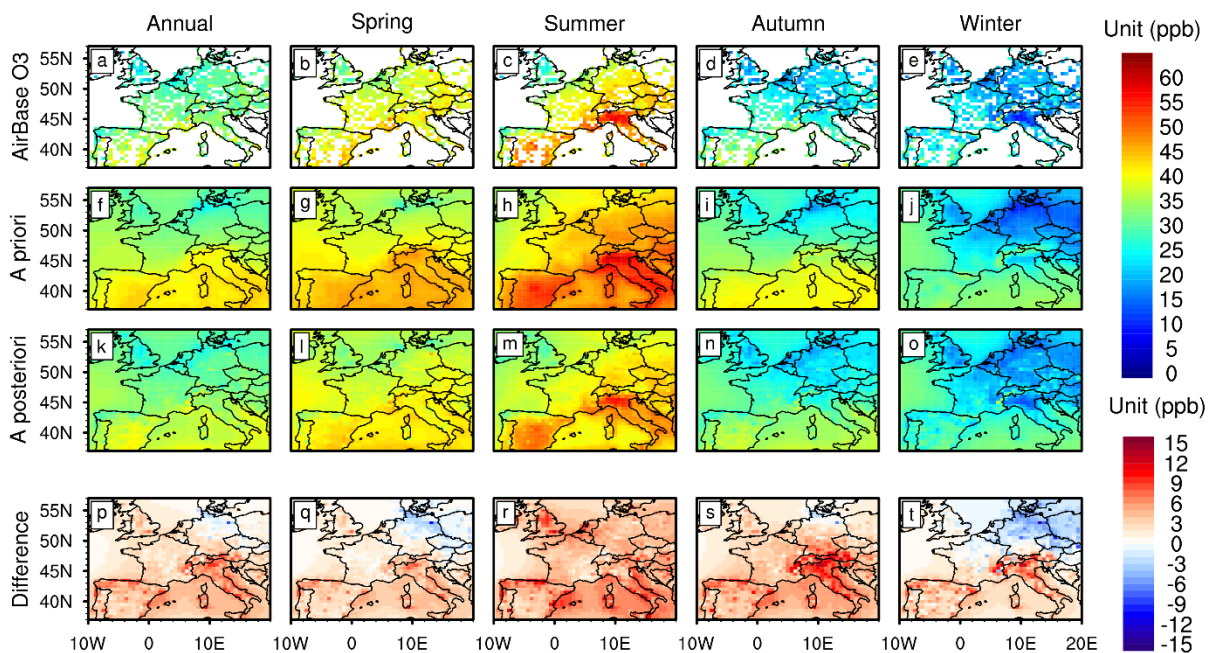| Europe			Annual		Spring		Summer		Autumn		Winter	
			Mean	Trend	Mean	Trend	Mean	Trend	Mean	Trend	Mean	Trend
T2.1 surface (sampled)	2005-2020	AirBase	31.6±0.2	0.08±0.04	38.5±0.1	-0.02±0.06	40.7±0.2	0.01±0.11	25.7±0.2	0.14±0.05	21.4±0.2	0.22±0.05
		a priori	35.3±0.2	0.04±0.03	40.3±0.2	-0.07±0.04	46.6±0.2	-0.07±0.09	31.5±0.2	0.07±0.05	22.9±0.2	0.24±0.05
		KF-AirBase	32.0±0.1	0.05±0.04	38.5±0.1	-0.04±0.06	41.3±0.2	-0.03±0.10	26.6±0.2	0.09±0.05	21.7±0.1	0.19±0.04
T2.2 surface	2005-2020	a priori	35.5±0.1	0.01±0.02	40.3±0.1	-0.10±0.04	46.0±0.2	-0.09±0.08	31.8±0.2	0.04±0.04	23.9±0.2	0.21±0.05
		KF-AirBase	32.5±0.1	0.01±0.03	38.5±0.1	-0.08±0.04	41.1±0.2	-0.08±0.09	27.7±0.1	0.04±0.04	22.8±0.1	0.17±0.04
T2.3 trop. column (convolved)	2005-2020	OMI	36.4±0.1	-0.15±0.06	37.6±0.1	-0.33±0.14	41.0±0.1	-0.09±0.08	34.5±0.1	-0.12±0.07	32.5±0.1	-0.09±0.11
		a priori	32.8±0.1	-0.09±0.03	33.6±0.1	-0.18±0.06	37.3±0.1	-0.14±0.06	31.3±0.1	-0.03±0.02	29.0±0.0	-0.02±0.05
		KF-OMI	35.3±0.1	-0.25±0.04	37.0±0.1	-0.40±0.09	40.5±0.1	-0.16±0.06	33.1±0.1	-0.22±0.04	30.4±0.0	-0.23±0.05
T2.4 trop. Column	2005-2020	a priori	32.1±0.1	0.03±0.03	33.7±0.1	-0.03±0.06	37.2±0.1	0.06±0.05	29.5±0.1	0.01±0.04	27.9±0.0	0.06±0.05
		KF-AirBase	31.5±0.1	0.03±0.03	33.3±0.1	-0.03±0.06	36.2±0.1	0.06±0.05	28.8±0.1	0.01±0.04	27.7±0.1	0.06±0.05
		KF-OMI	35.9±0.1	-0.36±0.04	39.5±0.1	-0.48±0.07	41.4±0.1	0.02±0.06	32.1±0.1	-0.38±0.05	30.4±0.0	-0.58±0.11
	2005-2009	KF-AirBase	31.2±0.1	-0.24±0.08	33.1±0.0	-0.17±0.26	35.8±0.1	-0.39±0.12	28.6±0.0	-0.40±0.21	27.3±0.0	-0.22±0.30
		KF-OMI	38.1±0.0	-0.38±0.22	41.6±0.1	-0.35±0.39	40.9±0.1	-0.06±0.23	34.6±0.0	-0.76±0.33	34.9±0.0	-1.06±0.44
	2010-2014	KF-AirBase	31.4±0.1	-0.24±0.23	33.6±0.0	-0.58±0.46	35.8±0.1	-0.33±0.32	28.7±0.1	-0.02±0.30	27.4±0.0	-0.16±0.34
		KF-OMI	35.7±0.1	-0.82±0.12	40.6±0.1	-1.30±0.25	41.6±0.1	-0.54±0.33	31.5±0.1	-0.40±0.19	28.3±0.0	-0.69±0.27
	2015-2020	KF-AirBase	31.7±0.1	0.03±0.09	33.1±0.1	-0.03±0.20	36.8±0.1	0.00±0.22	28.9±0.1	0.09±0.13	28.2±0.0	-0.02±0.20
		KF-OMI	34.3±0.1	-0.26±0.11	36.9±0.1	-0.58±0.14	41.6±0.1	-0.28±0.33	30.5±0.1	-0.19±0.15	28.5±0.0	-0.11±0.20

Table. 2. Averages (with units ppb or DU) and trends (with units ppb yr^{-1} or DU yr^{-1}) of surface and tropospheric column O$_3$ concentrations in 2005-2020 over Europe from observations (AirBase and OMI) and a priori and a posteriori (KF) simulations. T2.1): the modeled surface O$_3$ are sampled at the locations and times of AirBase surface O$_3$ observations; T2.2): the modeled surface O$_3$ are averaged over Europe (land only); T2.3): the output O$_3$ profiles from the a priori and a posteriori simulations are convolved with OMI O$_3$ averaging kernels; T2.4): the output O$_3$ profiles are NOT convolved with OMI O$_3$ averaging kernels.
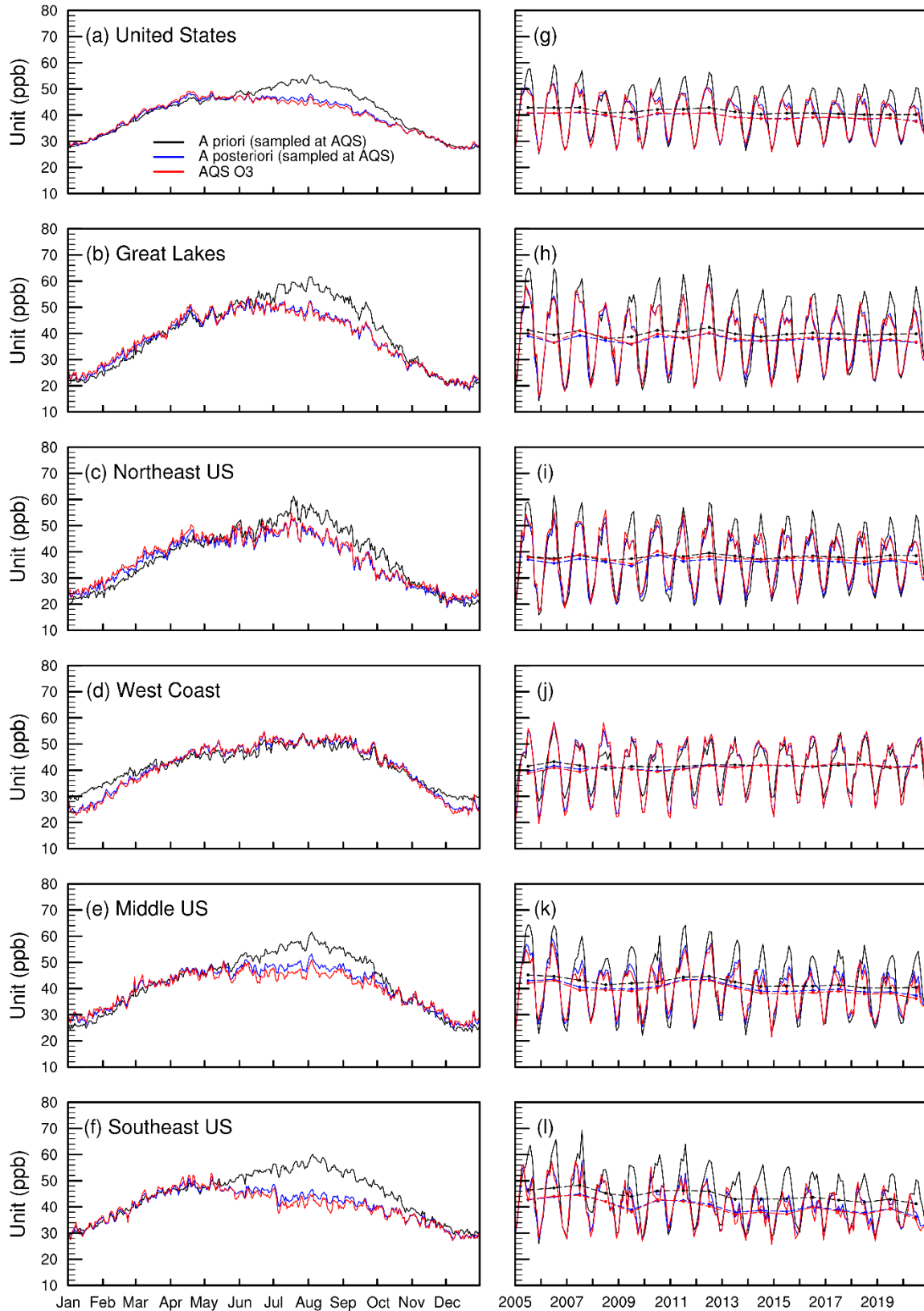
Fig. 1. (a) Anthropogenic NO_x emissions over the US in 2015; (b) Region definitions for Great Lakes (#1), Northeast US (#2), West Coast (#3), Middle US (#4) and Southeast US (#5). Regions #1-3 are defined as highly polluted (HP) regions by excluding grids with low and medium anthropogenic NO_x emissions. (c) Anthropogenic NO_x emissions over Europe in 2015; (d) Region definitions for Britain (#1), Central EU (#2), Western EU (#3), Iberian Peninsula (#4) and Apennine Peninsula (#5). Regions #1 and #2 are defined as highly polluted (HP) regions by excluding grids with low and medium anthropogenic NO_x emissions. The different colors (red, gray and green) represent grids with high (highest 15%), medium (15-50%) and low (lowest 50%) anthropogenic NO_x emissions.

Fig. 2. Surface MDA8 O_3 over the US in 2005-2020 (annual and seasonal averages) from (a-e) AQS stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AQS O_3 observations. (p-t) Bias in the a priori simulations calculated by a priori minus a posteriori O_3 concentrations.
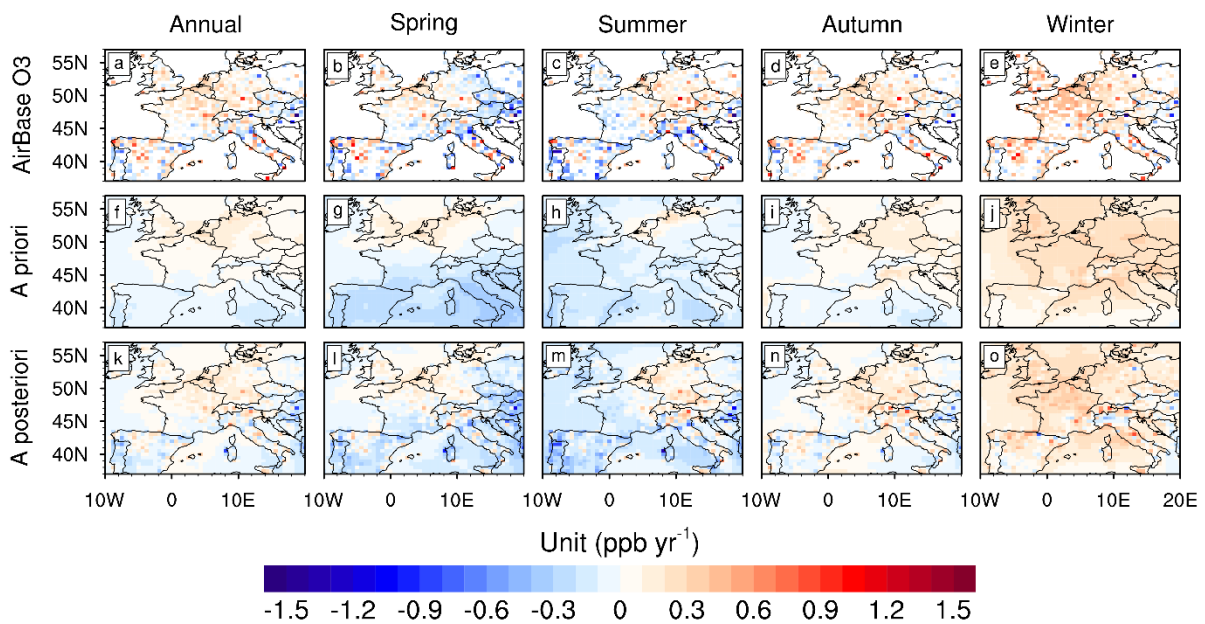

Fig. 3. Surface MDA8 O_3 over Europe in 2005-2020 (annual and seasonal averages) from (a-e) AirBase stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AirBase O_3 observations. (p-t) Bias in the a priori simulations calculated by a priori minus a posteriori O_3 concentrations.

Fig. 4. (a-f) Daily averages of surface MDA8 O_3 over the US in 2005-2020 from AQS stations (red) and GEOS-Chem a priori (black) and a posteriori (blue) simulations by assimilating AQS O_3 observations. (g-l) Monthly averages of MDA8 O_3. The dashed lines in panels g-l are annual averages.
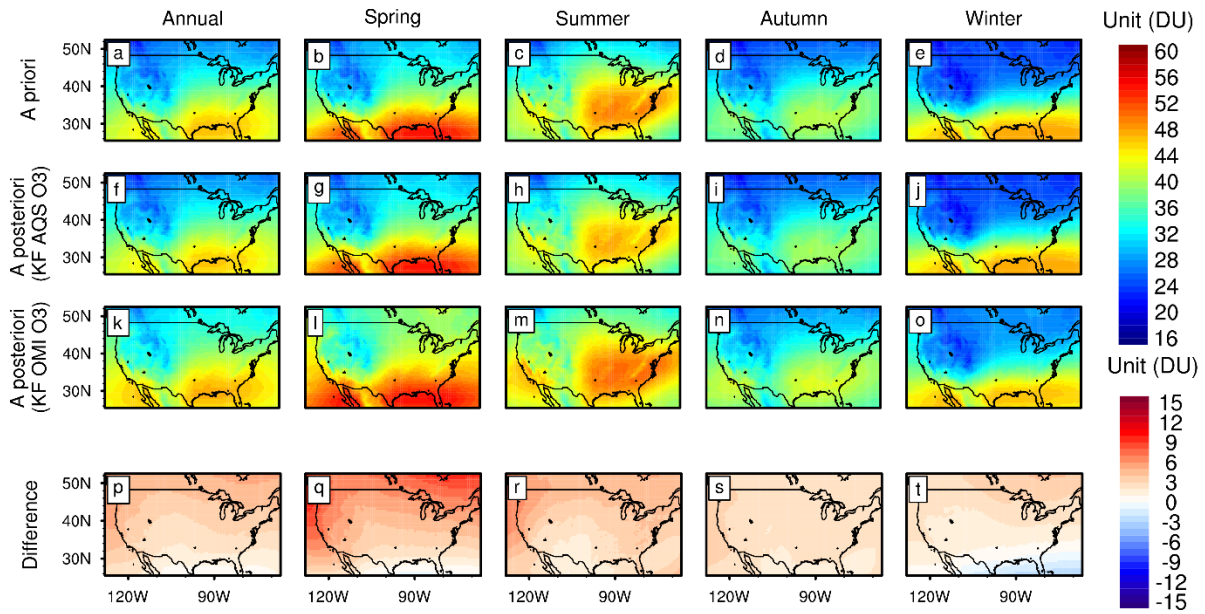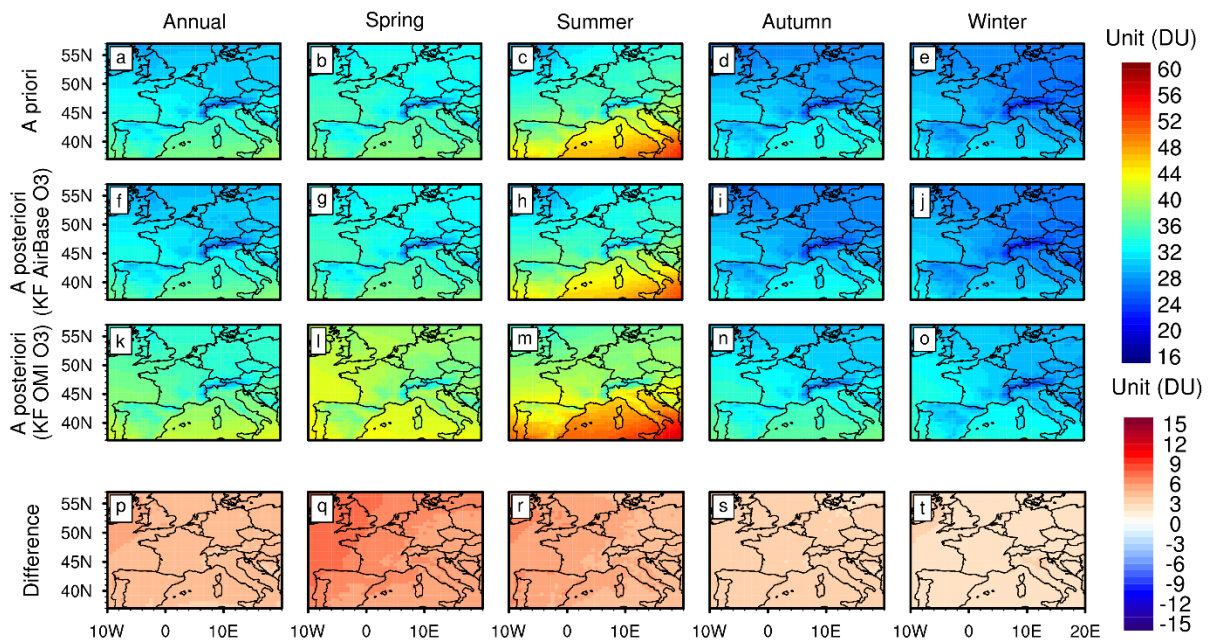
Fig. 5. (a-f) Daily averages of surface MDA8 O$_3$ over Europe in 2005-2020 from AirBase stations (red) and GEOS-Chem a priori (black) and a posteriori (blue) simulations by assimilating AirBase O$_3$ observations. (g-l) Monthly averages of MDA8 O$_3$. The dashed lines in panels g-l are annual averages.

Fig. 6. Trends of surface MDA8 O_3 over the US in 2005-2020 (annual and seasonal averages) from (a-e) AQS stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AQS O_3 observations.
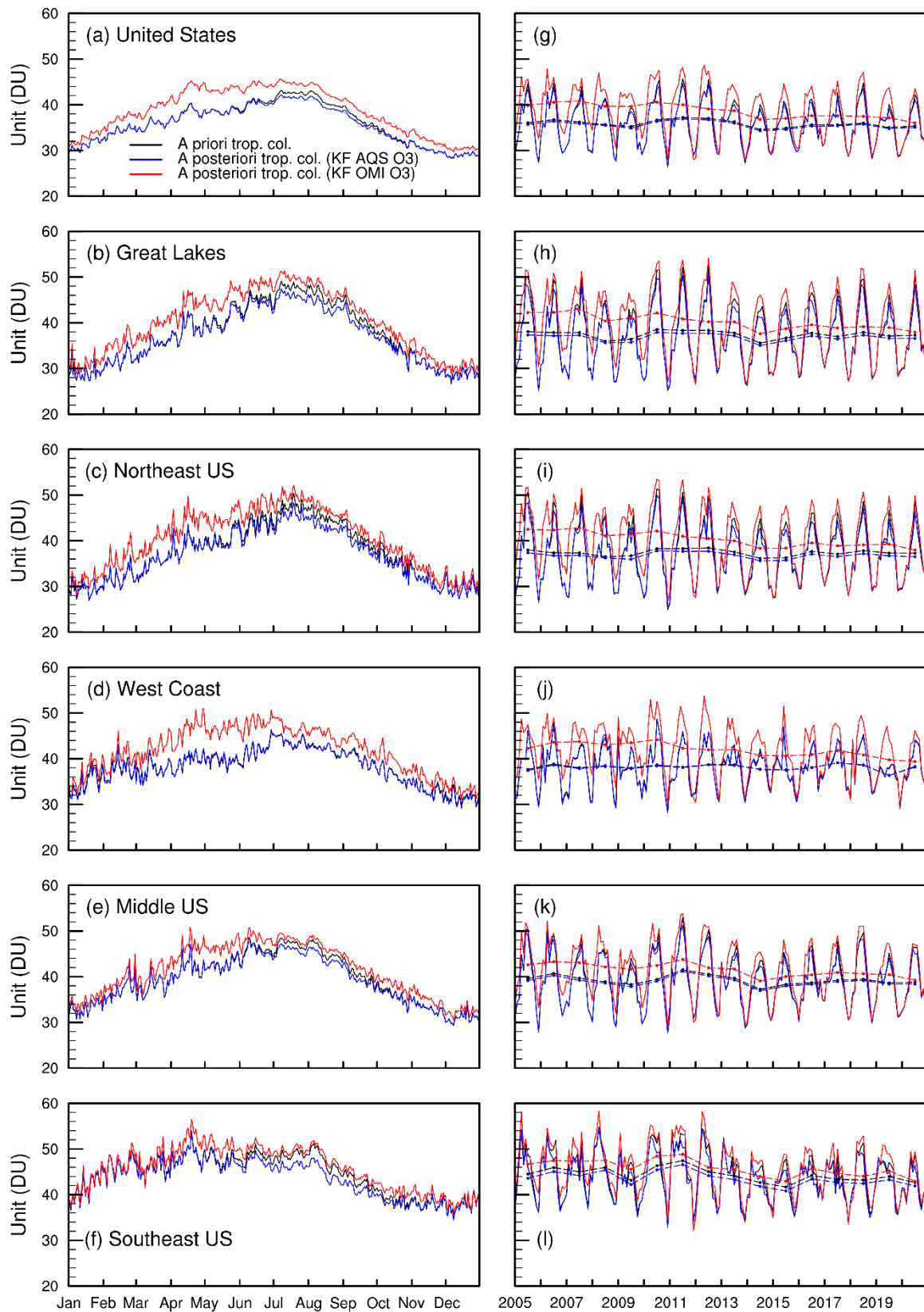

Fig. 7. Trends of surface MDA8 O_3 over Europe in 2005-2020 (annual and seasonal averages) from (a-e) AirBase stations; (f-j) GEOS-Chem a priori simulation; (k-o) GEOS-Chem a posteriori simulation by assimilating AirBase O_3 observations.

Fig. 8. Tropospheric O$_3$ columns over the US in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AQS surface O$_3$ observations; (k-o) Assimilations of OMI O$_3$ observations. (p-t) Difference in tropospheric O$_3$ columns calculated by OMI-based assimilations minus surface observation-based assimilations.
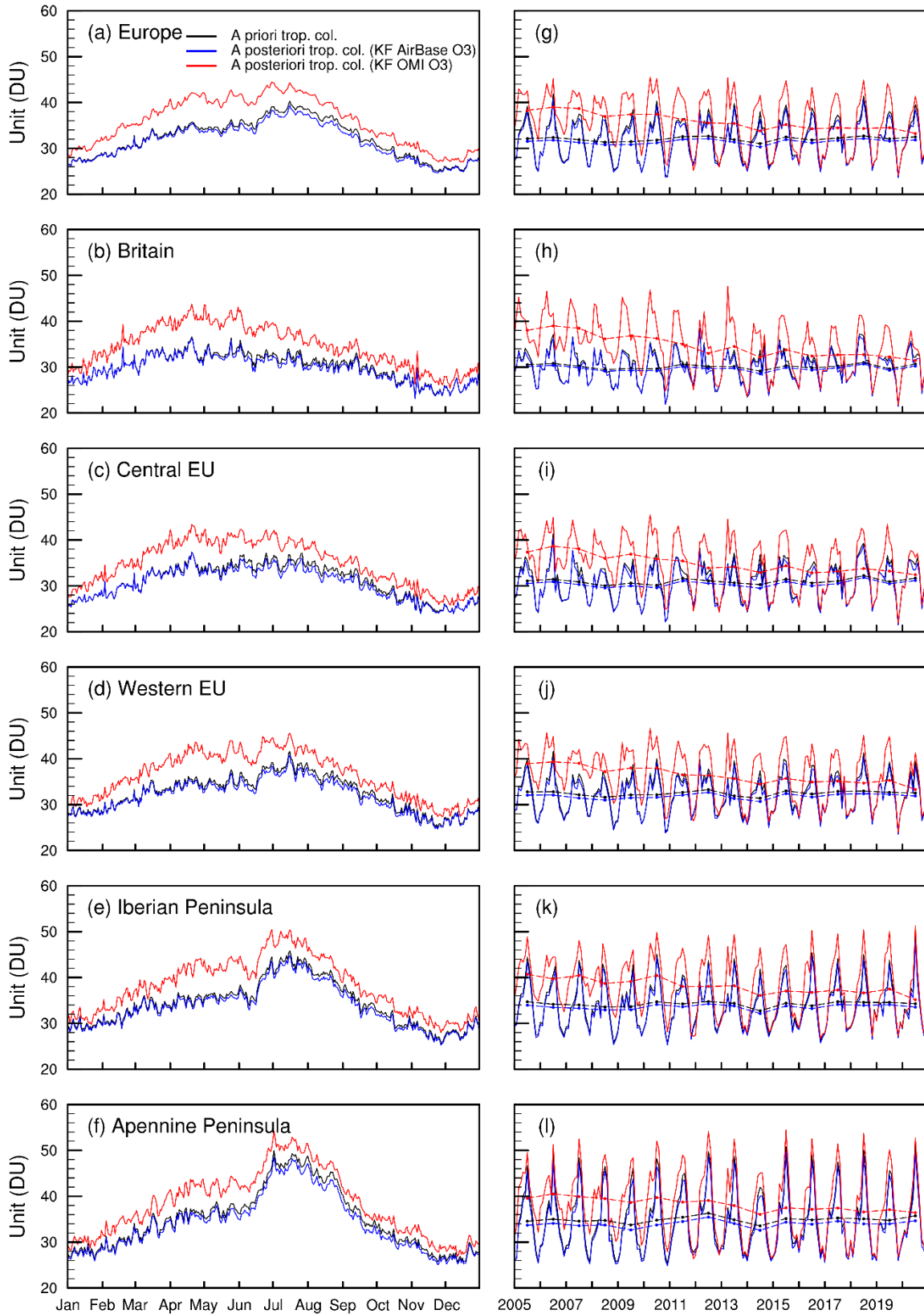

Fig. 9. Tropospheric O$_3$ columns over Europe in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AirBase surface O$_3$ observations; (k-o) Assimilations of OMI O$_3$ observations. (p-t) Difference in tropospheric O$_3$ columns calculated by OMI-based assimilations minus surface observation-based assimilations.
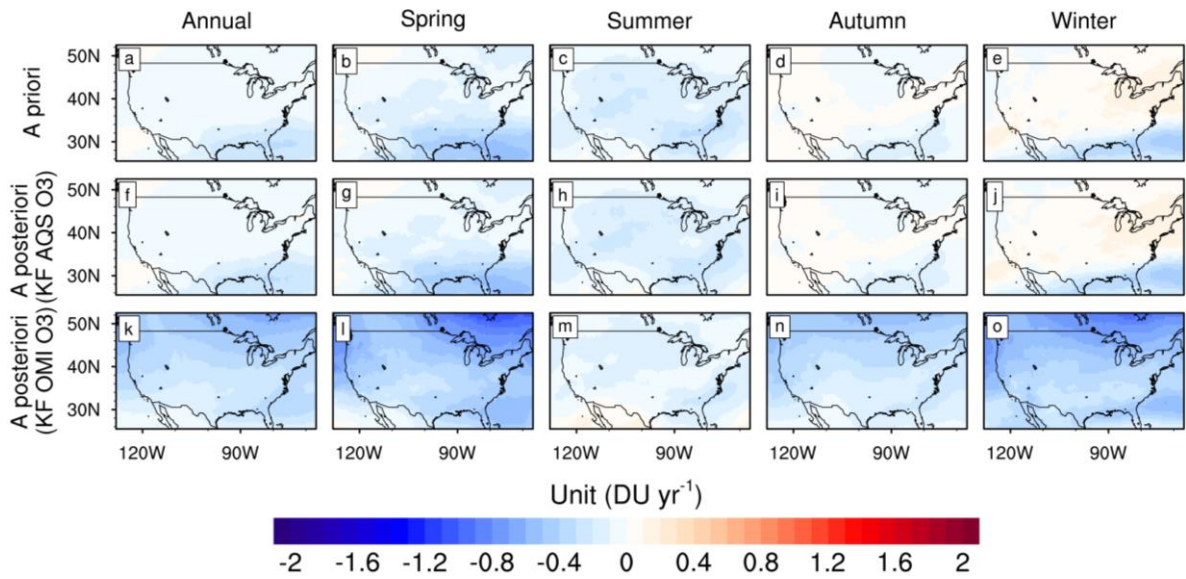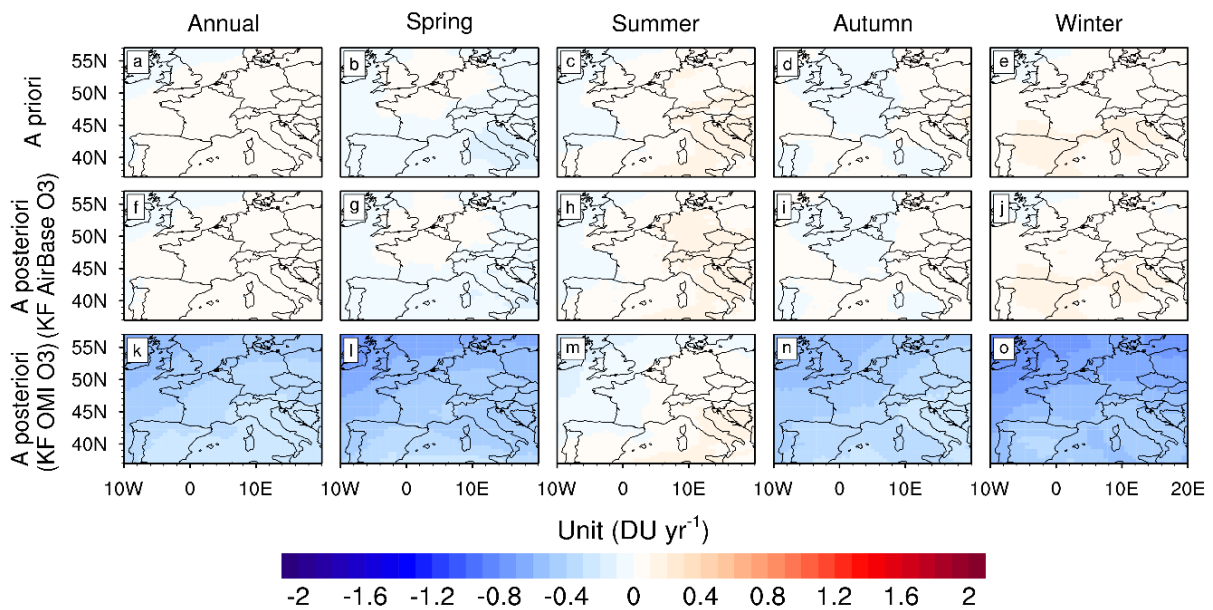
Fig. 10. (a-f) Daily averages of tropospheric O_3 columns over the US in 2005-2020 from GEOS-Chem a priori simulation (black) and a posteriori simulations by assimilating AQS (blue) and OMI (red) O_3 observations. (g-l) Monthly averages of tropospheric O_3 columns. The dashed lines in panels g-l are annual averages.

Fig. 11. (a-f) Daily averages of tropospheric O$_3$ columns over Europe in 2005-2020 from GEOS-Chem a priori simulation (black) and a posteriori simulations by assimilating AirBase (blue) and OMI (red) O$_3$ observations. (g-l) Monthly averages of tropospheric O$_3$ columns. The dashed lines in panels g-l are annual averages.

Fig. 12. Trends of tropospheric O₃ columns over the US in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AQS surface O₃ observations; (k-o) Assimilations of OMI O₃ observations.

Fig. 13. Trends of tropospheric O₃ columns over Europe in 2005-2020 (annual and seasonal averages) from (a-e) GEOS-Chem a priori simulation; (f-j) Assimilations of AirBase surface O₃ observations; (k-o) Assimilations of OMI O₃ observations.