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

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US and Europe and advises more efforts to evaluate the possible contributions of natural sources and transport. The discrepancy in assimilated tropospheric O_3 columns further indicates the possible uncertainties in the derived tropospheric O_3 changes.

1. Introduction

The successful emission regulations employed in the United States (US) and Europe (Crippa et al., 2016; EPA, 2017) have led to dramatic decreases in anthropogenic NO_x emissions (Di et al., 2020; Macdonald et al., 2021; Jiang et al., 2022). As an important air pollutant, tropospheric ozone (O_3) is produced when volatile organic compounds (VOCs) are photochemically oxidized in the presence of nitrogen oxides (NO_x). As a major precursor of tropospheric O_3, decreases in surface nitrogen dioxide (NO_2) concentrations, driven by declines in NO_x emissions, have led to marked decreases in surface O_3 concentrations over the US and Europe in recent decades. For example, Chen et al. (2021) found a decrease in surface O_3 concentrations from approximately 60 to 45 ppb over the US in 1990-2019; Seltzer et al. (2020) exhibited a decreasing trend of surface O_3 by approximately 0.8 ppb yr^{-1} over the US in 2000-2015; and Yan et al. (2018) found a decreasing trend of surface O_3 concentrations by approximately 0.32 $\mu g/m^3/y$ over Europe in 1995-2014.

While NO_x emissions are declining, the shift of NO_x sources from power generation to industrial and transportation sectors has led to diminishing effects on NO_x emission controls (Jiang et al., 2022). Furthermore, recent studies have demonstrated a slowdown in tropospheric NO_2 column declines with respect to surface NO_2 concentrations over the US since approximately 2010 (Jiang et al., 2018; Laughner and Cohen, 2019; Qu et al., 2021). Jiang et al. (2022) further indicated a slowdown of declines in tropospheric NO_2 columns with respect to surface NO_2 concentrations over both the US and Europe. Unlike surface O_3, which is strongly affected by local emissions, free tropospheric O_3 is more susceptible to the influences

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of free tropospheric sources and sinks, long-range transport, and stratospheric intrusion (Jiang et al., 2015; Xue et al., 2021; Trickl et al., 2020). The different trends in surface and free tropospheric NO_2 may thus result in different changes in surface and free tropospheric O_3 over the US and Europe.

A single O_3 tracer mode (tagged-O_3) of the GEOS-Chem model was developed in the companion paper (Zhu et al., 2023), and was combined with Ozone Monitoring Instrument (OMI) and surface O_3 observations in China in 2015-2020 via a sequential Kalman filter (KF) assimilation system (Tang et al., 2022; Han et al., 2022). The rapid O_3 assimilation capability with approximately 91-94% reductions in computational costs (Zhu et al., 2023) provides a new opportunity to extend atmospheric O_3 observations and mitigate the influence of uncertainties in physical and chemical processes (Li et al., 2019; Chen et al., 2022) and emission inventories (Zheng et al., 2017; Jiang et al., 2022). As the second part of this work, we assimilate OMI and US Air Quality System (AQS) and European AirBase network O_3 observations in this work to constrain tropospheric O_3 in the US and Europe in 2005-2020 with a 0.5°×0.625° horizontal resolution. A comparative analysis by assimilating satellite and surface O_3 observations is useful for better characterization of O_3 changes in the surface and free troposphere. Furthermore, this analysis helps evaluate the long-term performance of the GEOS-Chem model in simulating tropospheric O_3 and can provide new insights into tropospheric O_3 changes accompanied by the reported changes in tropospheric NO_2.

This paper is organized as follows: in Section 2, we provide descriptions for the AQS, AirBase and OMI O_3 observations and the single O_3 tracer simulation and assimilation system used in this work. We refer the reader to the companion paper (Zhu et al., 2023) for more details about the atmospheric O_3 observations and the development and performance of the single O_3 tracer assimilation system. Tropospheric O_3 changes in the US and Europe in 2005-2020 are demonstrated in Section 3 by assimilating atmospheric O_3 observations. As shown in Fig. 1,

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five regions (i.e., Great Lakes (#1), Northeast US (#2), West Coast (#3), Middle US (#4) and Southeast US (#5)) are defined within the US domain, and five regions (i.e., Britain (#1), Central EU (#2), Western EU (#3), Iberian Peninsula (#4) and Apennine Peninsula (#5)) are defined within the European domain based on anthropogenic NO_x emissions in 2015. Regions #1-3 (US) and regions #1-2 (Europe) are defined as highly polluted regions by excluding grids with low and medium anthropogenic NO_x emissions. Tropospheric O_3 changes over these regions will be discussed to investigate the possible regional discrepancies in surface and free tropospheric O_3 changes associated with different local pollution levels. Our conclusions follow in Section 4.

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2. Data and Methods

2.1 OMI and surface O_3 measurements

The OMI O_3 profile retrieval product (PROFOZ v0.9.3, level 2, Liu et al., 2010; Huang et al., 2017) from the Smithsonian Astrophysical Observatory (SAO) was assimilated in this work. The OMI instrument provides global covered measurements with backscattered sunlight in the ultraviolet–visible range from 270 to 500 nm (UV1: 270–310 nm; UV2: 310–365 nm; visible: 350–500 nm) with a spatial resolution of 13 × 24 km (nadir view). Following Huang et al. (2017), the following filters are applied: 1) nearly clear-sky scenes with effective cloud fraction < 0.3; 2) solar zenith angles (SZA) < 75°; and 3) fitting root mean square (RMS, ratio of fitting residuals to assumed measurement error) < 2.0. Starting in 2009, anomalies were found in OMI data and diagnosed as attenuated measured radiances in certain cross-track positions. This instrument degradation has been referred to as the "row anomaly". To enhance the quality and stability of data, only across-track positions between 4-11 (within 30 positions in the UV1 channels) are used in our analysis. This treatment is similar to the production of row-isolated data by using across-track positions between 3-18 (within 60 positions in the UV2

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

We use in situ hourly surface O_3 measurements from the US AQS and European Environment Agency AirBase networks. The AQS and AirBase networks collect ambient air pollution data from monitoring stations located in urban, suburban, and rural areas. To ensure the long-term stability of the observation record, we only considered stations with at least 14 years of observation records in 2005-2020. Observations provided by the AQS and AirBase stations have been widely used in previous studies to investigate the sources and variabilities of surface O_3 pollution (Shen et al., 2015; Boleti et al., 2020; He et al., 2022).

2.2 Single O_3 tracer simulation and assimilation system

The GEOS-Chem chemical transport model (http://www.geos-chem.org, version 12-8-1) is driven by assimilated meteorological data of MERRA-2. The GEOS-Chem full chemistry simulation includes fully coupled O_3-NO_x-VOC-halogen-aerosol chemistry. Our analysis is conducted at a horizontal resolution of nested 0.5°×0.625° over the US and Europe with chemical boundary conditions archived every 3 hours from global simulations with 4°×5° resolution. Emissions are computed by the Harvard-NASA Emission Component (HEMCO). Global default anthropogenic emissions are from the CEDS (Community Emissions Data System) (Hoesly et al., 2018). Regional emissions are replaced by MEIC (Multiresolution Emission Inventory for China) in China, MIX in other regions of Asia (Li et al., 2017) and NEI2011 in the US. Open fire emissions are from the Global Fire Emissions Database (GFED4) (van der Werf et al., 2010).

Following Jiang et al. (2022), the total anthropogenic NO_x and VOC emissions in the GEOS-Chem model are scaled with the corresponding bottom-up inventories (MEIC for China, NEI2014 for the US and ECLIPSE for Europe) so that the modeled surface nitrogen dioxide (NO_2) and VOC concentrations in the a priori simulations are identical to Jiang et al. (2022) in 2005-2018. The total anthropogenic NO_x and VOC emissions in 2019-2020 in China, the US

and Europe are further scaled based on linear projections. The total anthropogenic NO_x emissions in the a priori simulations declined by 53% (US) and 50% (Europe) in 2005-2020. The total anthropogenic VOC emissions in the a priori simulations declined by 19% (US) and 33% (Europe) in 2005-2020. We refer the reader to Jiang et al. (2022) for the details of the model configuration and performance, particularly the modeled trends of surface and tropospheric column NO_2 in 2005-2018.

A new single O_3 tracer mode (tagged-O_3) was developed in the companion paper (Zhu et al., 2023) by reading the archived production (PO3) and loss (LO3) of O_3 provided by the full chemistry simulation. The major advantage of the single O_3 tracer mode is dramatic reductions in computational costs by approximately 91-94% (Zhu et al., 2023). Fig. S1 and Fig. S2 (see the SI) show the annual and seasonal averages of surface maximum daily 8-hour average (MDA8) O_3 over the US and Europe in 2005-2020 from the full chemistry and single O_3 tracer simulations (i.e., the a priori simulations in this work), respectively. We find good spatial (Fig. S1 and Fig. S2) as well as temporal (Fig. S3, see the SI) consistencies in surface MDA8 O_3 between full chemistry and single O_3 tracer simulations over the US and Europe in 2005-2020. The computation costs (hours of wall time for one year simulation) are 160.7 and 9.4 hours within the nested US domain (0.5°×0.625°) and 103.4 and 6 hours within the nested Europe domain (0.5°×0.625°) by full chemistry and single O_3 tracer mode, respectively.

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The low computational costs of the single O_3 tracer mode allow us to perform O_3 assimilations more efficiently. The sequential KF was conducted to assimilate AQS, AirBase and OMI O_3 observations to produce the a posteriori O_3 concentrations. As a brief description of the assimilation algorithm, the forward model ($\mathbf{M}$) predicts the O_3 concentration ($\boldsymbol{x}_{at}$) at time t:

$$\boldsymbol{x}_{at} = \mathbf{M}_t \boldsymbol{x}_{t-1} \quad \text{(Eq. 1)}$$

The optimized O_3 concentrations can be expressed as:

$$\boldsymbol{x}_t = \boldsymbol{x}_{\mathrm{at}} + \mathbf{G}_t(\boldsymbol{y}_t - \mathbf{K}_t\boldsymbol{x}_{\mathrm{at}}) \quad (\mathrm{Eq.}\,2)$$

where $\boldsymbol{y}_t$ is the observation (i.e., OMI or surface O_3 observations) and $\mathbf{K}_t$ represents the operation operator that projects O_3 concentrations from the model space to the observation space. $\mathbf{G}_t$ is the KF gain matrix, which can be described as:

$$\mathbf{G}_t = \mathbf{S}_{\mathrm{at}}\mathbf{K}_t^T(\mathbf{K}_t\mathbf{S}_{\mathrm{at}}\mathbf{K}_t^T + \mathbf{S}_\epsilon)^{-1} \quad (\mathrm{Eq.}\,3)$$

where $\mathbf{S}_{\mathrm{at}}$ and $\mathbf{S}_\epsilon$ are the model and observation covariances, respectively. The modeled tropospheric O_3 profiles in the OMI-based assimilation processes are convolved by using the OMI retrieval averaging kernels. The mixing of O_3 precursors in the planetary boundary layer is considered with a simplified planetary boundary layer parameterization in surface observation-based assimilations. We refer the reader to the companion paper (Zhu et al., 2023) for more details about the development and performance of the single O_3 tracer assimilation system by assimilating satellite and surface O_3 observations.

3. Results and Discussion

3.1 Surface O_3 by assimilating surface O_3 observations

Fig. 2a-e and Fig. 3a-e show the annual and seasonal averages of surface MDA8 O_3 observations from US AQS and European AirBase stations in 2005-2020. Fig. 2k-o and Fig. 3k-o further show the annual and seasonal averages of the a posteriori O_3 concentrations by assimilating AQS or AirBase O_3 observations. As shown in Fig. 4 and Fig. 5, the assimilated O_3 concentrations (blue lines) show good agreements with surface O_3 observations (red lines): the mean surface MDA8 O_3 in 2005-2020 are 41.4, 39.5 and 39.5 ppb (US), 40.0, 37.7 and 38.2 ppb (Great Lakes), 38.1, 36.4 and 37.4 ppb (Northeast US), 41.6, 41.2 and 41.0 ppb (West Coast), 42.2, 40.4 and 39.7 ppb (Middle US), 44.4, 40.3 and 39.9 ppb (Southeast US) in the a priori simulations, a posteriori simulations and AQS observations, respectively; the mean

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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 (Britain), 30.5, 28.2 and 28.0 ppb (Central EU), 35.9, 32.5 and 32.3 ppb (Western EU), 40.3, 35.2 and 34.2 ppb (Iberian Peninsula), 41.8, 35.3 and 34.0 ppb (Apennine Peninsula) in the a priori simulations, a posteriori simulations and AirBase observations, respectively.

Similar to China, we find overestimated summertime surface O_3 concentrations in the a priori simulations over the US and Europe (Fig. 4 and Fig. 5). However, in contrast to the underestimated O_3 declines in June-July in China (Zhu et al., 2023), the overestimated summertime O_3 over the US and Europe are caused by overestimated increases in surface O_3 in July-August, which have led to surface MDA8 O_3 maximum in July-August in the simulations. In contrast, assimilations suggest that surface O_3 is broadly maximum in April over the US and Europe (Fig. 4 and Fig. 5), although O_3 seasonality varies over different regions. We find good agreements in surface O_3 concentrations between a priori and a posteriori simulations over the US in seasons outside of summer (Fig. 2p-t), in contrast to the large differences between a priori and a posteriori simulations over Europe (Fig. 3p-t in this work) and China (Zhu et al., 2023). The inaccurate surface O_3 concentrations over three continents reveal possible uncertainties in model simulations, particularly the contributions from natural and anthropogenic processes; for example, the higher temperature and solar radiation can lead to high O_3 concentrations in August, whereas the transport of O_3 and its precursors can lead to high O_3 concentrations in April (Parrish et al., 2013).

Furthermore, our analysis exhibits high surface MDA8 O_3 concentrations over the West Coast (41.2 ppb) in the US. Except for the West Coast, the assimilated surface MDA8 O_3 concentrations are lower over areas with higher anthropogenic NO_x emissions over the US and Europe. For example, 37.7 and 36.4 ppb in the Great Lakes and Northeast US, respectively, in contrast to 40.4 and 40.3 ppb in the Middle US and Southeast US, respectively; and 26.0 and 28.2 ppb in the Britain and Central EU, respectively, in contrast to 32.5, 35.2 and 35.3 ppb in

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the Western EU, Iberian Peninsula and Apennine Peninsula, respectively. The inverse relationships between surface O_3 concentrations and local anthropogenic NO_x emissions indicate the important impacts of natural sources and meteorological conditions on surface O_3 pollution over the US and Europe because of continuous declines in anthropogenic emissions in the past decades. This is the opposite of the higher O_3 concentrations in areas with higher local anthropogenic NO_x emissions in China (Zhu et al., 2023), where surface O_3 pollution is strongly affected by anthropogenic emissions.

3.2 Limited changes in surface O_3 concentrations

Following Jiang et al. (2022), the anthropogenic NO_x and VOC emissions over the US in 2005-2020 declined by 53% (-5.1% yr^{-1}) and 19% (-1.4% yr^{-1}) in our a priori simulations, which is accompanied by slight decreasing trends in surface MDA8 O_3 in the a priori simulations (Table 1.1): -0.29 (spring), -0.45 (summer), -0.07 (autumn) and 0.05 (winter) ppb yr^{-1}; and the relative trends are -0.7 (spring), -0.9 (summer), -0.2 (autumn) and 0.2 (winter) % yr^{-1}. Similarly, the anthropogenic NO_x and VOC emissions over Europe in 2005-2020 declined by 50% (-4.4% yr^{-1}) and 33% (-2.7% yr^{-1}) in our a priori simulations, which is accompanied by slightly increasing trends of surface MDA8 O_3 in the a priori simulations (Table 2.1): -0.07 (spring), -0.07 (summer), 0.07 (autumn) and 0.24 (winter) ppb yr^{-1}; and the relative trends are -0.2 (spring), -0.2 (summer), 0.2 (autumn) and 1.0 (winter) % yr^{-1}. It is surprising to see the limited changes in surface O_3 concentrations in the simulations accompanied by dramatic declines in anthropogenic emissions.

We thus further investigate the changes in surface O_3 by assimilating surface O_3 observations. As shown in Table 1.1 and Fig. 6k-o, our assimilations suggest -0.27 (spring), -0.46 (summer), -0.12 (autumn) and 0.11 (winter) ppb yr^{-1} changes in surface MDA8 O_3 over the US in 2005-2020, and the relative changes are -0.6 (spring), -1.0 (summer), -0.3 (autumn) and 0.4 (winter) % yr^{-1}. Similarly, as shown in Table 2.1 and Fig. 7k-o, our assimilations

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suggest -0.04 (spring), -0.03 (summer), 0.09 (autumn) and 0.19 (winter) ppb yr^{-1} changes in surface MDA8 O_3 over Europe in 2005-2020, and the relative changes are -0.1 (spring), -0.1 (summer), 0.3 (autumn) and 0.9 (winter) % yr^{-1}. In contrast to the underestimated increasing trends in surface O_3 concentrations in the a priori simulations in China (Zhu et al., 2023), we find broadly consistent trends between simulations and assimilations over the US and Europe, which confirms the limited changes in surface O_3 concentrations over the US and Europe.

The changes in surface O_3 concentrations have marked regional and seasonal discrepancies. As shown in Tables S1-S5 (see the SI), our assimilations demonstrate stronger increasing trends in surface O_3 concentrations in 2005-2020 in the winter (0.39 ppb yr^{-1} or 1.5% yr^{-1}) over the Great Lakes, in the winter (0.36 ppb yr^{-1} or 1.4% yr^{-1}) over the Northeast US, in 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 Coast, as well as decreasing trends in surface O_3 concentrations in 2005-2020 in the summer 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}), 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 areas with higher anthropogenic NO_x emissions such as the Great Lakes and Northeast US demonstrate lower surface O_3 concentrations and are accompanied by stronger increasing trends in the winter and weaker decreasing trends in the summer.

Tables S6-S10 (see the SI) further show the details of tropospheric O_3 changes in Europe. Our assimilations demonstrate stronger increasing trends in surface O_3 concentrations in 2005-2020 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% 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}) and Apennine Peninsula (0.18 ppb yr^{-1} or 0.8% yr^{-1}), as well as decreasing trends in surface O_3 concentrations in 2005-2020 in the summer (-0.07 ppb yr^{-1} or -0.2% yr^{-1}) over Britain, in the summer (-0.10 ppb yr^{-1} or -0.2% yr^{-1}) over the Western EU, in the summer (-0.20 ppb yr^{-1} or -0.5% yr^{-1}) over the Iberian Peninsula and in the spring (-0.09 ppb yr^{-1} or -0.2% yr^{-1}) over the

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Apennine Peninsula. Similar to the US, areas with higher anthropogenic NO_x emissions such as Britain and Central EU demonstrate lower surface O_3 concentrations and are accompanied by stronger increasing trends in the winter and weaker decreasing trends in the summer.

Furthermore, Zhu et al. (2023) demonstrated a large discrepancy in the trends in assimilated surface O_3 between urban (i.e., areas with air quality stations) and regional backgrounds in China in 2015-2020: 3.0% yr^{-1} (sampled at air quality stations) and 1.3% yr^{-1} (land average). In contrast, we did not find a comparable discrepancy over the US and Europe: the trends of assimilated surface O_3 are -0.4% yr^{-1} (Table 1.1, sampled at AQS O_3 observations) and -0.4% yr^{-1} (Table 1.2, land average) over the US and -0.2% yr^{-1} (Table 2.1, sampled at AirBase O_3 observations) and 0.0% yr^{-1} (Table 2.2, land average) over Europe. The difference between China and the US/Europe suggests more consistent changes in surface O_3 between urban and regional background areas in the US and Europe. This implies possible larger relative contributions of regional background O_3 to surface O_3 observations in the US and Europe, which could be associated with the limited changes in surface O_3 concentrations in 2005-2020 because regional background O_3 is less sensitive to changes in anthropogenic NO_x and VOC emissions.

3.3 Tropospheric O_3 columns by assimilating OMI O_3 observations

Fig. S4a-e and Fig. S5a-e (see the SI) show the annual and seasonal averages of tropospheric OMI O_3 columns in 2005-2020 over the US and Europe, respectively. Fig. S4k-o and Fig. S5k-o further show the annual and seasonal averages of the a posteriori tropospheric O_3 columns by assimilating OMI O_3 observations. The assimilated tropospheric O_3 columns show good agreement with OMI O_3 observations: the mean tropospheric O_3 columns over the US in 2005-2020 (Table 1.3) are 35.5 DU in the a priori simulations, and 37.0 and 36.8 DU in the a posteriori simulations and OMI observations, respectively; the mean tropospheric O_3 columns over Europe in 2005-2020 (Table 2.3) are 32.8 DU in the a priori simulations, and

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35.3 and 36.4 DU in the a posteriori simulations and OMI observations, respectively. However, there are small deviations in the trends between assimilations and OMI observations. As shown in Fig. S6-S7 (see the SI), the trends of tropospheric O_3 columns over the US in 2005-2020 (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 posteriori simulations and OMI observations, respectively; the trends of tropospheric O_3 columns over Europe in 2005-2020 (Table 2.3) are -0.09 DU yr^{-1} in the a priori simulations, and -0.25 and -0.15 DU yr^{-1} in the a posteriori simulations and OMI observations, respectively. These deviations are associated with the adjustments to regional O_3 boundary conditions in the nested assimilations by assimilating global OMI O_3 observations, reflecting the different changes in OMI O_3 between US/Europe continents and global backgrounds. For example, the mean tropospheric O_3 columns over the US in 2005 are 36.5 DU in OMI observations, and 35.9 and 37.5 DU in the assimilations by reading a priori and adjusted O_3 boundary conditions, respectively; the mean tropospheric O_3 columns over Europe in 2005 are 37.5 DU in OMI observations, and 34.6 and 36.9 DU in the assimilations by reading a priori and adjusted O_3 boundary conditions, respectively.

The annual averages of surface MDA8 O_3 in the a priori simulation and assimilations are 35.3 and 32.0 ppb with a relative difference of 10% over Europe (Table 2.1); 41.4 and 39.5 ppb with a relative difference of 5% over the US (Table 1.1); and 42.9 and 41.8 ppb with a relative difference of 3% over China (Zhu et al., 2023). In addition, the annual averages of tropospheric O_3 columns in the a priori simulation and assimilations are 32.8 and 35.3 DU with a relative difference of -7% over Europe (Table 2.3); 35.5 and 37.0 DU with a relative difference of -4% over the US (Table 1.3); and 37.1 and 37.9 DU with a relative difference of -2% over China (Zhu et al., 2023). It seems that the GEOS-Chem model has a better performance in regional averages of surface and free tropospheric O_3 concentrations in China and the US than in Europe.

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The output O_3 profiles from a priori and a posteriori simulations are convolved with OMI averaging kernels in Fig. S4-S7. However, the convolution of OMI O_3 averaging kernels on the output O_3 profiles can affect the weights of the derived tropospheric columns to O_3 at different vertical levels and thus may not accurately represent the actual tropospheric O_3 columns. Fig. 8 and Fig. 9 further show tropospheric O_3 columns from a priori and a posteriori simulations, in which the output O_3 profiles are not convolved with OMI averaging kernels. The assimilated tropospheric O_3 columns are 35.6 and 38.7 DU (US), 36.8 and 40.2 DU (Great Lakes), 36.8 and 40.3 DU (Northeast US), 38.1 and 41.9 DU (West Coast), 38.9 and 41.5 DU (Middle US), 43.5 and 45.8 DU (Southeast US) in 2005-2020 by assimilating AQS and OMI O_3 observations, respectively; the assimilated tropospheric O_3 columns are 31.5 and 35.9 DU (Europe), 29.7 and 34.7 DU (Britain), 30.4 and 34.9 DU (Central EU), 31.8 and 36.4 DU (Western EU), 33.6 and 38.1 DU (Iberian Peninsula), 34.0 and 38.2 DU (Apennine Peninsula) in 2005-2020 by assimilating AirBase and OMI O_3 observations, respectively. We find that tropospheric O_3 columns obtained by assimilating surface O_3 observations are lower than those obtained by assimilating OMI O_3 observations. Similar to surface O_3 concentrations, tropospheric O_3 columns are lower over areas with higher anthropogenic NO_x emissions over the US and Europe such as the Great Lakes, Northeast US, Britain and Central EU. This is opposite to the higher tropospheric O_3 columns over areas with higher local anthropogenic NO_x emissions in China (Zhu et al., 2023).

In contrast to the surface MDA8 O_3 maximum in April in the observations (Fig. 4 and Fig. 5), the assimilated tropospheric O_3 columns are broadly maximum in July-August over the US and Europe (Fig. 10 and Fig. 11). The free tropospheric O_3 maximum in the summer has been reported in previous studies. For example, Wespes et al. (2018) demonstrated a free tropospheric O_3 maximum in summer over Europe by using Infrared Atmospheric Sounding Interferometer (IASI) observations; Petetin et al. (2016) exhibited a free tropospheric O_3

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maximum in summer over Europe by using MOZAIC aircraft measurements. We find good agreement in the seasonality of free tropospheric O_3 between simulations and assimilations in contrast to the inaccurate simulation of the seasonality of surface O_3 concentrations in the simulations. More studies are needed in the future to explore the sources of this difference in model performance.

Furthermore, Fig. S8-S9 (see the SI) demonstrate the O_3 vertical profiles in 2005-2009, 2010-2014 and 2015-2020, respectively. The assimilation of surface O_3 observations leads to decreases in O_3 concentrations in the lower troposphere but has small impacts on free tropospheric O_3. In contrast, the assimilation of OMI O_3 observations leads to dramatic enhancements in O_3 concentrations in the middle and upper troposphere without noticeable differences between areas with high and low local anthropogenic NO_x emissions. The enhancement in free tropospheric O_3 by assimilating OMI O_3 observations declined gradually from 2005-2009 to 2015-2020. The adjustment in free tropospheric O_3 by assimilating OMI O_3 observations in 2015-2020 is larger but comparable with the adjustment in 2015-2020 in China (Zhu et al., 2023).

3.4 Large decreases in tropospheric O_3 columns

Fig 12 and Fig. 13 show the trends in tropospheric O_3 columns in 2005-2020 from a priori simulations and a posteriori simulations by assimilating surface and OMI O_3 observations. The trends of tropospheric O_3 columns in 2005-2020 are -0.07, -0.07 and -0.29 DU yr^{-1} (US), -0.03, -0.03 and -0.29 DU yr^{-1} (Great Lakes), -0.02, -0.02 and -0.31 DU yr^{-1} (Northeast US), -0.02, -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 and -0.28 DU yr^{-1} (Southeast US) in the a priori simulations and a posteriori simulations by assimilating AQS and OMI O_3 observations, respectively; and are 0.03, 0.03 and -0.36 DU yr^{-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), 0.02, 0.03 and -0.36 DU yr^{-1} (Western EU), 0.02, 0.02 and -0.30 DU yr^{-1} (Iberian Peninsula), -

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0.04, 0.04 and -0.26 DU yr^{-1} (Apennine Peninsula) in the a priori simulations and a posteriori simulations by assimilating AirBase and OMI O_3 observations, respectively. Our analysis thus exhibits dramatically lower decreasing trends in tropospheric O_3 columns in the a priori simulations and assimilations by assimilating surface O_3 observations with respect to OMI-based assimilations.

The limited changes in surface O_3 concentrations in the a priori simulations and assimilations by assimilating surface O_3 observations indicate limited influences of declines in local anthropogenic emissions on surface O_3 concentrations in the US and Europe in 2005-2020. We can thus expect insignificant influences of the vertical transport of surface O_3 on the changes in free tropospheric O_3 over the US and Europe in 2005-2020, as illustrated by the flat trends in tropospheric O_3 columns in the a priori simulations and assimilations by assimilating surface O_3 observations (Fig. 10 and Fig. 11), as well as the small impacts of assimilation of surface O_3 observations on free tropospheric O_3 (Fig. S8-S9). However, as indicated by Jiang et al. (2022), tropospheric OMI NO_2 columns declined by 36% and 23% in 2005-2018 over the US and Europe, respectively. Are the large decreases in tropospheric O_3 columns by assimilating OMI O_3 observations, i.e., 12.0% (US) and 15.0% (Europe) in 2005-2020, caused by the declines in free tropospheric NO_2?

As indicated by Jiang et al. (2022), tropospheric OMI NO_2 columns declined by -7.0% yr^{-1} (US) and -4.2% yr^{-1} (Europe) in 2005-2010, which was followed by a dramatic slowdown in the decreasing trends, i.e., -1.7% yr^{-1} (US) and -1.2% yr^{-1} (Europe) in 2010-2018. However, as shown in Table 1.4, tropospheric O_3 columns obtained by assimilating OMI O_3 observations declined by -0.3, -2.3 and -0.5% yr^{-1} over the US in 2005-2009, 2010-2014 and 2015-2020, respectively. Similarly, tropospheric O_3 columns obtained by assimilating OMI O_3 observations declined by -1.0, -2.3 and -0.8% yr^{-1} over Europe (Table 2.4) in 2005-2009, 2010-2014 and 2015-2020, respectively. The OMI-based declines in tropospheric O_3 columns over

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the US and Europe mainly occurred in the period with slowed decreases in free tropospheric NO_2 after 2010; in contrast, the dramatic declines in tropospheric NO_2 columns before 2010 were accompanied by limited changes in free tropospheric O_3. It is thus difficult to conclude that the large decreases in tropospheric O_3 columns over the US and Europe in 2010-2014 are dominated by declines in local anthropogenic NO_x emissions.

We note our OMI-based analysis could be affected by the row anomaly issue, although the usage of "row-isolated" data by using across-track positions between 4-11 in this work is expected to reduce the impacts of row anomaly. As shown by Huang et al. (2017), the row anomaly can lead to discontinuity in the trends in OMI O_3 observations in 2009. However, the large decreases in tropospheric O_3 columns over the US and Europe mainly occurred after 2010. Consequently, we assume a limited influence of row anomaly on our conclusion. Furthermore, OMI is sensitive to O_3 concentrations in the free troposphere; OMI-based assimilations are driven by adjusted regional O_3 boundary conditions provided by global OMI O_3 assimilations and can reflect optimized adjustments in both local and global background O_3 concentrations. In contrast, surface observations are sensitive to local O_3 concentrations; surface observation-based assimilations are driven by the a priori O_3 boundary conditions, which thus reflects the optimized adjustments in local contributions and is also affected by lacking optimization on the impacts of O_3 precursors due to the single O_3 tracer simulations. These factors contributed to the difference in the trends of tropospheric O_3 columns by assimilating surface and satellite observations. Assimilations of both surface and satellite observations, as shown in this work, are expected to provide more information to better characterization of the changes and uncertainties in free tropospheric O_3.

4. Conclusion

As a companion paper of Zhu et al. (2023) which focuses on tropospheric O_3 change in China in 2015-2020, this paper investigates the changes in surface and free tropospheric O_3

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over the US and Europe in 2005-2020 by assimilating OMI, AQS and AirBase 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) in the a priori and a posteriori simulations and AQS and AirBase O_3 observations, respectively; and tospheric 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 a priori and a posteriori simulations (convolved with OMI retrieval averaging kernels) and OMI O_3 observations, respectively. The modeled surface O_3 by GEOS-Chem is overestimated in the summer, which results in a surface O_3 maximum in July-August in the simulations in contrast to April in the observations; in contrast, GEOS-Chem demonstrates good performance in the simulation of seasonality in free tospheric O_3, which is maximum in July-August. In addition, we find lower surface O_3 concentrations over areas with higher anthropogenic NO_x emissions in the US and Europe. This is the opposite of the higher O_3 concentrations in areas with higher local anthropogenic NO_x emissions in China (Zhu et al., 2023).

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Our analysis exhibits a noticeable decrease in surface O_3 concentrations over the US in the summer by 15% in 2005-2020. However, accompanied by approximately 50% reductions in NO_x emissions, changes in surface O_3 concentrations are limited in Europe and other seasons in the US: the annual surface MDA8 O_3 decreased by -6% over the US and increased by 1.5% over Europe in 2005-2020, and the decreases in surface O_3 concentrations are weaker over areas with higher local anthropogenic NO_x emissions. Furthermore, the surface observation-based assimilations suggest insignificant changes in tospheric O_3 columns: -3.0% (US) and 1.5% (Europe) in 2005-2020. While the OMI-based assimilations exhibit large decreases in tospheric O_3 columns, i.e., -12.0% (US) and -15.0% (Europe) in 2005-2020, the decreases in tospheric O_3 columns mainly occurred in 2010-2014, corresponding to reported slowed declines in free tospheric NO_2 since 2010 (Jiang et al., 2022). Despite the dramatic declines

in tropospheric NO_2, particularly, declines in tropospheric NO_2 columns in 2005-2010, our analysis suggests limited impacts of local emission declines on changes in tropospheric O_3 over the US and Europe because the rapid decline in tropospheric NO_2 columns in 2005-2010 corresponds to relatively flat trends in tropospheric O_3. More efforts are suggested to evaluate the contributions of natural sources and transport to tropospheric O_3 changes, which is critical for making more effective policies to reduce O_3 pollution.

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Code and data availability: The AQS and AirBase surface O_3 data can be downloaded from https://www.eea.europa.eu/data-and-maps/data/aqereporting-8 and https://aqs.epa.gov/aqsweb/airdata/download_files.html#Row. The OMI PROFOZ product can be acquired at https://avdc.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L2/OMPROFOZ/. The GEOS-Chem model (version 12.8.1) can be downloaded from http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_12#12.8.1. The KPP module for tagged-O_3 simulations can be downloaded from https://doi.org/10.5281/zenodo.7545944.

Competing interests: The contact author has declared that neither they nor their co-authors have any competing interests.

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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

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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

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Deleted: K-O) GEOS-Chem a posteriori simulation by assimilating OMI O_3 observations. The output O_3 profiles are convolved with OMI averaging kernels.¶ ¶ **Fig. 8.** Tropospheric O_3 columns in 2005-2020 (annual and seasonal averages) from (A-E) GEOS-Chem a priori simulation; (F-J) assimilations
Deleted: or AirBase
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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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