

# Earth and Space Science



## RESEARCH ARTICLE

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### Key Points:

- In middle and low thermosphere of below ~300 km, storm-time decreases of the ratio of O/N<sub>2</sub> volume density are mainly caused by O reduction
- In the upper thermosphere, N<sub>2</sub> enhancement plays a vital role in the decreases of the ratio of O/N<sub>2</sub> volume density during the storm
- At all pressure levels, storm-time increases of the ratio of O/N<sub>2</sub> volume density depend more on the N<sub>2</sub> decreases

### Supporting Information:

Supporting Information may be found in the online version of this article.

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## Vertical Variations in Thermospheric O/N<sub>2</sub> and the Relationship Between O and N<sub>2</sub> Perturbations During a Geomagnetic Storm

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**Abstract** The ratio of O to N<sub>2</sub> number densities (O/N<sub>2</sub>) at different altitudes is an important parameter in describing thermospheric neutral composition changes and their effects on the ionosphere during geomagnetic storms. However, storm-induced vertical variations in O/N<sub>2</sub> and its dependence on the O and N<sub>2</sub> perturbations are still not fully understood. Here, the Thermosphere/Ionosphere Electrodynamics General Circulation Model simulations were used to investigate the responses of thermospheric composition at different pressure levels to the super geomagnetic storm occurred on November 20 and 21 in 2003. Our analysis shows that the behaviors of O/N<sub>2</sub> perturbations on different pressure levels are similar above ~180 km altitude. In the middle and low thermosphere of below ~300 km, the storm-time O/N<sub>2</sub> decrease is mainly caused by a large reduction of O number density. However, N<sub>2</sub> enhancement plays a vital role in O/N<sub>2</sub> decreases in the upper thermosphere. The O/N<sub>2</sub> enhancement is mainly attributed to the N<sub>2</sub> decreases at all pressure levels. The changes of O and N<sub>2</sub> number densities at a constant pressure level can be explained by the perturbations of their mass mixing ratio (mmr) and total mass density ( $\rho$ ). The regions of the O/N<sub>2</sub> decrease are characterized by the O mmr decrease and N<sub>2</sub> mmr enhancement, whereas the regions of the O/N<sub>2</sub> increase are characterized by the O mmr increase and N<sub>2</sub> mmr decrease. The  $\rho$  value that shows the decrease globally at most pressure levels during the storm either enhance or reduce the O and N<sub>2</sub> perturbations.

**Plain Language Summary** The column O/column N<sub>2</sub> density ratio ( $\sum O/N_2$ ) was usually used to describe thermospheric neutral composition responses to geomagnetic storms and the storm effects on ionospheric plasma density. However, thermospheric circulation changed considerably during the storm, resulting in discrepancies in composition at different altitudes. Additionally, the daytime electron density changes during geomagnetic storms are more related to those of local O/N<sub>2</sub> at a given altitude, not the  $\sum O/N_2$ . Therefore, it is important to fully understand the storm-induced vertical variations in O, N<sub>2</sub> and O/N<sub>2</sub> perturbations. In this paper, the vertical variations in O/N<sub>2</sub> and its dependence on the O and N<sub>2</sub> perturbations during the 20–21 November 2003 storm are investigated by the numerical simulations. Our results shows that the behaviors of O and N<sub>2</sub> perturbations depend much on the altitude, but those of O/N<sub>2</sub> on different pressure levels are similar, especially above ~180 km. This study helps us better understand the physical process of storm-time  $\sum O/N_2$  variations based on the observations.

## 1. Introduction

The ratios of height-integrated number density of atomic oxygen (O) to that of molecular nitrogen (N<sub>2</sub>), namely column O/column N<sub>2</sub> density ratio ( $\sum O/N_2$ ), which can be deduced by disk-viewing optical observations of OI 135.6 nm and Lyman-Birge-Hopfield radiances (Meier, 2021; Strickland et al., 1995), has been widely utilized to describe thermospheric neutral composition responses to geomagnetic storms and the storm effects on ionospheric plasma density (e.g., Cai et al., 2020, 2021a, 2021b, 2023; Crowley et al., 2006; Eastes et al., 2020; Lee et al., 2013; Liou et al., 2005; Strickland et al., 1999, 2001; Wang et al., 2021; Yu et al., 2022a, 2022b; Zhai et al., 2023; Zhang et al., 2004). Previous studies demonstrated the evolution and physical processes of  $\sum O/N_2$  during geomagnetic storms, which is briefly summarized as follows. High-latitude Joule heating during a storm induces temperature changes, and causes upward winds and

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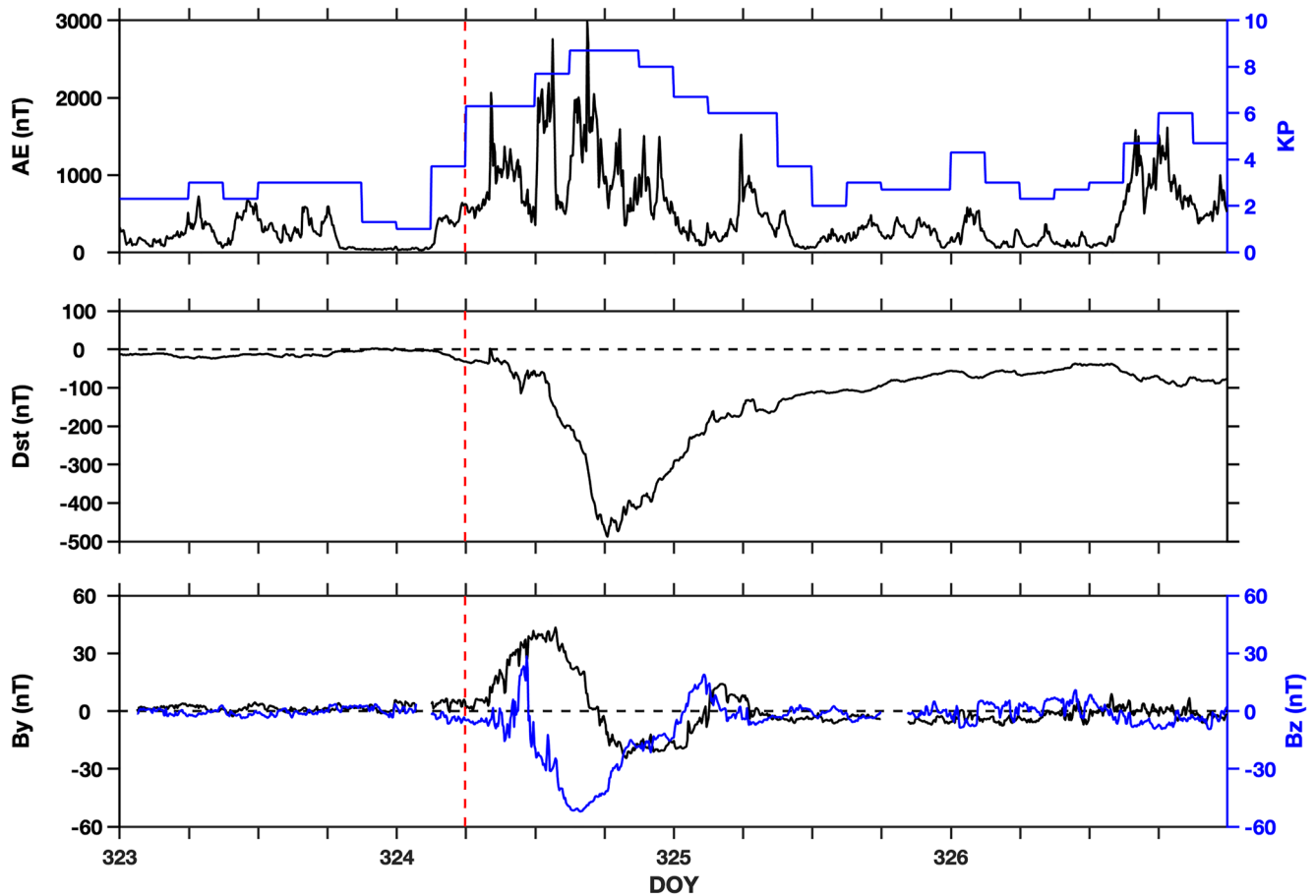
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upwelling of air such that the  $N_2$ -rich/O-poor air is brought up from the lower thermosphere ( $\sim 100$  km) into the  $F$  region (Burns, Killeen, Carignan, & Roble, 1995; Burns, Killeen, Deng et al., 1995; Fuller-Rowell et al., 1994). At the same time, high-latitude temperature enhancement results in a strong equatorward horizontal pressure gradient and enhanced equatorward neutral winds to transmit the  $N_2$ -rich/O-poor air to the mid-low latitudes. This seems to imply that the large  $N_2$  increases at high latitudes cause  $\Sigma O/N_2$  depletion, which then extends to mid-low latitudes as the storms proceed (Kil et al., 2013; Meier et al., 2015). On the other hand, downwelling of air occurs at lower latitudes adjacent to the high latitude upwelling region due to thermospheric storm-time circulation changes. This storm-time downwelling of O-rich/ $N_2$ -poor air increases  $\Sigma O/N_2$  (Burns, Killeen, Carignan, & Roble, 1995; Burns, Killeen, Deng et al., 1995; Immel et al., 2001; Kil et al., 2013).  $\Sigma O/N_2$  enhancement pattern is also propagated equatorward due to horizontal transport (Cai et al., 2022; Immel et al., 2008).

Other than  $\Sigma O/N_2$ , the ratio of O and  $N_2$  number densities at a particular altitude is defined as the ratio of O/ $N_2$  volume density (hereafter simply  $O/N_2$ ) (Yue et al., 2019). The daytime electron density changes during geomagnetic storms are more related to those of local  $O/N_2$  at a given altitude, not the  $\Sigma O/N_2$  (Crowley & Meier, 2008). This is because electron production is related to the photoionization of local O number density and its loss is proportional to local  $N_2$  number density (Rishbeth, 1998). Burns, Killeen, Carignan, and Roble (1995) and Burns, Killeen, Deng et al. (1995) investigated the storm-time responses of  $O/N_2$  at  $\sim 370$  km by using the in situ observations of the Dynamics Explorers 2 (DE 2) satellite and the Thermosphere/Ionosphere General Circulation Model.  $O/N_2$  enhancements were observed and simulated during the storm main phase in the middle latitudes in the winter hemisphere. They demonstrated that  $O/N_2$  increases are partially caused by the reduction of  $N_2$  number density.  $N_2$ -poor air was brought from higher thermosphere to lower thermosphere. In addition, there was a good correlation between the daytime  $O/N_2$  increases on a constant pressure level and daytime electron density enhancements at the  $F_2$  peak during the storm. Crowley and Meier (2008) also showed that the regions of storm-time  $O/N_2$  increases were consistent with those of electron density enhancements near the  $F$  layer peak.

These aforementioned previous studies focused on the  $O/N_2$  changes in the  $F$  region. Based on the Global Ultraviolet Imager (GUVI) limb measurements, Kil et al. (2011a) presented the altitude profiles of the perturbations in O,  $N_2$  and  $O/N_2$  during the 20 November 2003 superstorm at two selected geophysical locations in the height coordinates. The compositional changes in the height coordinates are affected by the thermal contraction and expansion (Burns, Killeen, Carignan, & Roble, 1995; Burns, Killeen, Deng et al., 1995). Kil et al. (2011a) concluded that the storm-time  $O/N_2$  perturbations in the  $F$  region were mostly determined by the  $N_2$  changes in the height coordinates. Furthermore, they found an inconsistency during the storm between the variations in  $O/N_2$  in the  $F$  region and those of  $\Sigma O/N_2$ . There were only minor changes in  $O/N_2$  in the  $F$  region where  $\Sigma O/N_2$  increases were observed. Yu et al. (2021a) use the GUVI limb retrievals to investigate the responses of O and  $N_2$  altitude profiles to the 20 November 2003 superstorm. The relative contributions of O and  $N_2$  changes to the  $O/N_2$  responses in the middle thermosphere ( $\sim 160$  km) were presented briefly. They stressed that during the storm main and recovery phases, the middle thermospheric ( $\sim 160$  km)  $O/N_2$  depletion on a constant pressure surface was mostly related to O decreases, whereas  $O/N_2$  enhancement depended primarily on  $N_2$  decreases.

However, GUVI instrument provides approximately 14 orbital data every day corresponding to different UTs/longitudes, thus does not provide global longitude-latitude distribution of neutral composition at a particular UT (Meier et al., 2015). In comparison, numerical simulations can provide storm-time composition perturbations globally for both day and night. Additionally, the previous studies have not fully understood the storm-induced  $O/N_2$  variations at different altitudes and their relationship with O and  $N_2$  perturbations, which are the subjects of this paper. Yu et al. (2021b) employed Thermosphere/Ionosphere Electrodynamics General Circulation Model (TIEGCM) simulations to study O and  $N_2$  responses on a constant pressure surface ( $z = -1.5$ ,  $\sim 160$  km) during the 20 November 2003 superstorm. Yu et al. (2021b) demonstrated that TIEGCM simulations qualitatively reproduced the GUVI observations. The model captures the large-scale structures of the composition changes during this superstorm, and its temporal evolution of the effects are coincident with the observations. Thus, the model is valuable to investigate the composition perturbations during this storm and can be used to gain insights into the possible physical mechanisms driving these changes. In this paper, based on the general consistency between GUVI measurements and TIEGCM results, we used TIEGCM simulations to further investigate the vertical variations of  $O/N_2$  and their relationship with O,  $N_2$  changes on a global scale during the 20 and 21 November 2003 (day of year (DOY) 324 and 325) superstorm.



**Figure 1.** The top panel is the variations of AE (black line) and 3-hr Kp (blue line) indices on day of year 323–326 in 2003; the second panel is the hourly Dst index, and the black dashed line is the zero value of the Dst index; the third panel is the y (By, black line) and z (Bz, blue line) component of the interplanetary magnetic field. The black dashed line is the zero value of By and Bz. The red dashed line indicates the storm onset time.

## 2. TIEGCM Simulation

The TIEGCM is a three-dimensional, time-dependent, global thermosphere-ionosphere model that can self-consistently simulate composition, dynamics, circulation, electrodynamics, photoionization and chemistry in the thermosphere from ~97 to 600 km (Richmond et al., 1992; Roble et al., 1988). The TIEGCM utilized a spherical coordinate system with longitude and latitude as the horizontal coordinates and pressure surfaces as the vertical coordinate. The version used here has a high horizontal resolution of  $1.25^\circ \times 1.25^\circ$  in geographic longitude and latitude, and a vertical resolution of 0.25 scale height. Solar EUV irradiance input and auroral electron precipitation input of the model are based on Solomon and Qian (2005) and Roble and Ridley (1987), respectively. The Heelis empirical model (Heelis et al., 1982) is used as the high-latitude input. The monthly tidal climatology (Hagan & Forbes, 2002, 2003) is used as the lower boundary input.

## 3. Results and Discussion

### 3.1. Geophysical Conditions

The variations of the geomagnetic activity indices from DOY 323 to 326 in 2003 are shown in Figure 1. On DOY 323, 3-hr Kp (blue line) index was less than 3, and AE (black line) index was less than ~500 nT (the top panel). The absolute values of the hourly Dst index (the second panel), and interplanetary magnetic field (IMF) By and Bz components (the third panel) were close to zero. Thus, DOY 323 was chosen as the quiet-time reference. Kp and AE indices started to increase sharply at ~6 UT on DOY 324 (red dashed line), and both the By and Bz components also began to change rapidly. This means the storm onset. The Kp and AE indices reached maxima

of 9° and ~3,000 nT at ~15 UT on DOY 324, and then decreased to the minima of 2 and ~100 nT at ~12 UT on DOY 325, respectively. During this period (~6 UT on DOY 324 to ~12 UT on DOY 325), Dst index decreased slowly from ~6 UT to ~12 UT on DOY 324. It then rapidly decreased from ~12 UT to reach a minimum of ~-490 nT at ~18–20 UT on DOY 324, and then began to recover. The IMF By component had negative values from ~17 UT on DOY 324 to ~3 UT on DOY 325, and was positive for the rest of the period. Bz remained southward (negative) for a long period of time, except for a few hours of northward at about 10–11 UT on DOY 324 and at ~1–5 UT on DOY 325. IMF By and Bz had large magnitudes of around 50 nT during the storm period. The magnitudes of these parameters became small from ~12 UT on DOY 325 until ~14 UT on DOY 326. According to the variations of the geomagnetic indices, the initial phase of the storm was from ~6 UT to ~12 UT on DOY 324. The storm main phase was approximately from ~12 UT to ~20 UT on DOY 324. The storm recovery phase began after that.

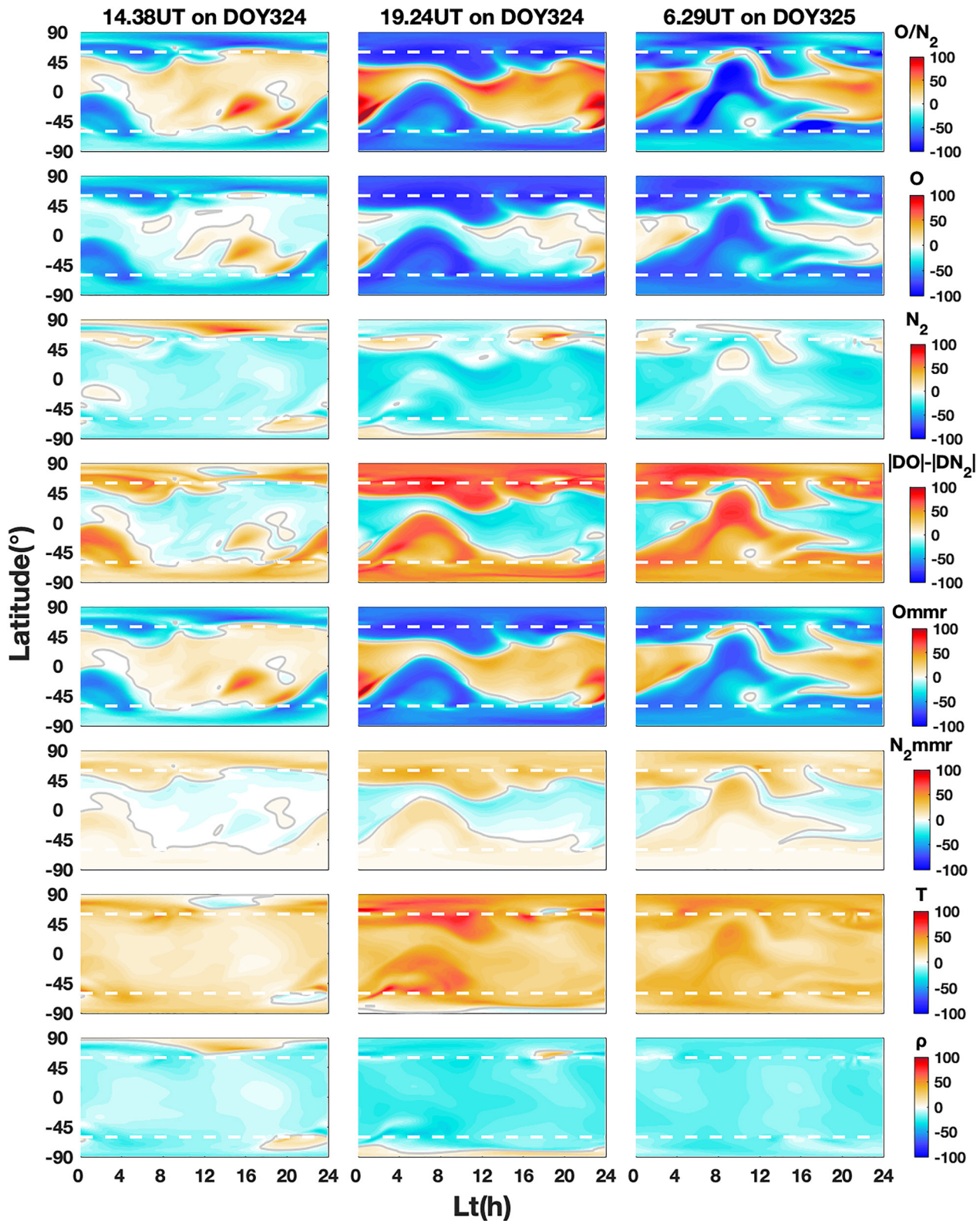
### 3.2. Composition Variations on the $z = -1.5$ Pressure Surface (~160 km)

Before the discussion of composition perturbations in vertical direction, we first present the modeled relative contributions of storm-time O and N<sub>2</sub> changes to the O/N<sub>2</sub> responses in the middle thermosphere ( $z = -1.5$  pressure surface at ~160 km in the TIEGCM simulation). We selected three UTs from the storm initial (14.38 UT on DOY 324), main (19.24 UT on DOY 324) and recovery (6.29 UT on DOY 325) phases to show the latitude and local time distribution of the storm-induced percentage changes ((storm-quiet)/quiet) in O/N<sub>2</sub>, O and N<sub>2</sub> number densities in Figure 2 (first -third rows). In addition, we calculated the differences of the absolute values of O and N<sub>2</sub> percentage changes to present their relative magnitudes in O/N<sub>2</sub> perturbations (the fourth row).

Figure 2 shows that in the pressure coordinate, the storm-time O can be either increased or decreased with different magnitudes in different longitude and latitude regions over the entire storm period. Whereas N<sub>2</sub> decreased almost in all regions on this pressure level over the entire storm period, except in some regions at high latitudes where N<sub>2</sub> had an enhancement. Comparing the changes between O, N<sub>2</sub> and O/N<sub>2</sub> in the regions of O/N<sub>2</sub> decreases shown in Figure 2 and in the pressure coordinates, we can see that during the initial phase of the storm, O decreased by ~30–60%. N<sub>2</sub> increased by about 20%–50% at high latitudes in the Northern Hemisphere (NH), but decreased in other regions by ~20%. During the main and recovery phases of the storm and in regions of O/N<sub>2</sub> decreases, O decreased by more than 100%, and N<sub>2</sub> decreased at most regions by ~5–40%. The differences between the absolute values of O and N<sub>2</sub> percentage changes in the fourth row are mostly greater than zero (0–~80%), which indicates that O had larger changes (reduction) relative to N<sub>2</sub> in the regions of O/N<sub>2</sub> depletion, though their changes depended on the longitude and latitude. Thus, O/N<sub>2</sub> decreases during the storm were primarily caused by a large O reduction on this constant pressure surface. It is worth noting that O/N<sub>2</sub> decreases in the summer Southern Hemisphere (SH) had an extended latitudinal range relative to those in the winter NH. The hemispheric asymmetry is partly due to the summer-to-winter prevailing circulation, meanwhile, there existed the more intensive Joule heating and ion drag in the summer SH, resulting in the stronger temperature gradients and equatorial wind perturbations in the SH (Fuller-Rowell et al., 1994; Yu et al., 2021a).

In the regions of O/N<sub>2</sub> enhancement, the composition responses during this superstorm are a bit more complicated. During the initial phase of the storm, N<sub>2</sub> decreased by ~10–20%, but O changes were close to zero except in two regions (~0°–~45° S, ~14–~18.5 LT; ~40°–~60° S, ~18–~21.5 LT) where O increased by ~30%. During the main and recovery phases, N<sub>2</sub> decreased by ~40–80% in the regions of O/N<sub>2</sub> increases. O was increased or decreased, but the magnitude was less than 20%. The differences between the absolute values of O and N<sub>2</sub> percentage changes were mostly negative (0–40%), which indicates a larger contribution of N<sub>2</sub> number density changes to O/N<sub>2</sub> increases in most regions. Therefore, the storm-induced O/N<sub>2</sub> enhancement in the middle thermosphere is primarily attributed to the large decreases of N<sub>2</sub>.

However, a larger O increase (~50%) was seen in the ~0°–~45° S latitudes near ~12–~17 LT in the SH during the storm initial phase. The differences between the absolute values of O and N<sub>2</sub> percentage changes were greater than zero, indicating the important effects of O to O/N<sub>2</sub> increases. Yu et al. (2021b) demonstrated that this O increase was due to the day-to-day variation of the thermosphere, mainly caused by the horizontal advection. Additionally, there was another larger O increase (~40%) occurred in the ~40°–~60° S latitude range near ~18–~21 LT in the storm initial phase. The two large O increases gradually merged and were transported to the ~0–~45° S latitude range near ~23–~2 LT in the storm main phase. The differences between the absolute values of O and N<sub>2</sub> percentage changes were near zero during the main phase in the region, which indicates that the



**Figure 2.** (top to bottom) Latitude and local time distributions of the percentage changes ((storm-quiet)/quiet) of  $O/N_2$ ,  $O$ , and  $N_2$  number densities, the differences of absolute value of  $O$  and  $N_2$  percentage changes,  $O$  mass mixing ratios ( $O$  mmr) and  $N_2$  mass mixing ratios ( $N_2$  mmr), temperature ( $T$ ) and total mass density ( $\rho$ ) on the  $z = -1.5$  (~160 km) pressure surface at three UTs (left to right). In each panel the gray curves indicate the zero value, and the two white dashed lines are the latitude of  $\pm 60^\circ$ .

O and N<sub>2</sub> changes are both important in determining the storm-time O/N<sub>2</sub> enhancement in this region. This O increase resulted from the downwelling at high latitudes and then were propagate to middle-low latitudes by the horizontal advection, referring to Movie S2 in Yu et al. (2021b). Therefore, the storm-induced O/N<sub>2</sub> enhancement in the middle thermosphere was dependent more on the large N<sub>2</sub> decreases, except in some regions where O/N<sub>2</sub> enhancement was dominated both by O and N<sub>2</sub> changes.

Next, we investigate the causes of the behaviors of O and N<sub>2</sub> number densities in the middle thermosphere through TIEGCM simulations. TIEGCM calculates the mass mixing ratio (mmr) of O and N<sub>2</sub> (O mmr,  $\Psi_o$  and N<sub>2</sub> mmr,  $\Psi_{N_2}$ ), and their relationship with the total air mass density can be described as the following:

$$\Psi_o = \rho_o / \rho \text{ (where } \rho_o = m_o n_o \text{)}$$

$$\Psi_{N_2} = \rho_{N_2} / \rho \text{ (where } \rho_{N_2} = m_{N_2} n_{N_2} \text{)} \quad (1)$$

where  $\rho_o$  is the O mass density with atomic mass  $m_o$ , and  $n_o$  is the O number density.  $\rho_{N_2}$  is the N<sub>2</sub> mass density with molecular mass  $m_{N_2}$ , and  $n_{N_2}$  is the N<sub>2</sub> number density.  $\rho$  is the total mass density. Therefore, the differential changes of O (N<sub>2</sub>) number density can be expressed as:

$$d\rho_o / \rho_o = dn_o / n_o = d\Psi_o / \Psi_o + d\rho / \rho$$

$$d\rho_{N_2} / \rho_{N_2} = dn_{N_2} / n_{N_2} = d\Psi_{N_2} / \Psi_{N_2} + d\rho / \rho \quad (2)$$

where  $d$  is the differential sign. The storm-quiet percentage changes ((storm-quiet)/quiet) of O (N<sub>2</sub>) number density can refer to Equation 2 to assess the contribution from their mass mixing ratios and the total mass density. Note that the differential equation is mainly valid for small changes, thus cannot be used to quantitatively estimate the storm-quiet changes. However, it is appropriate to evaluate their respective signs in Equation 2.

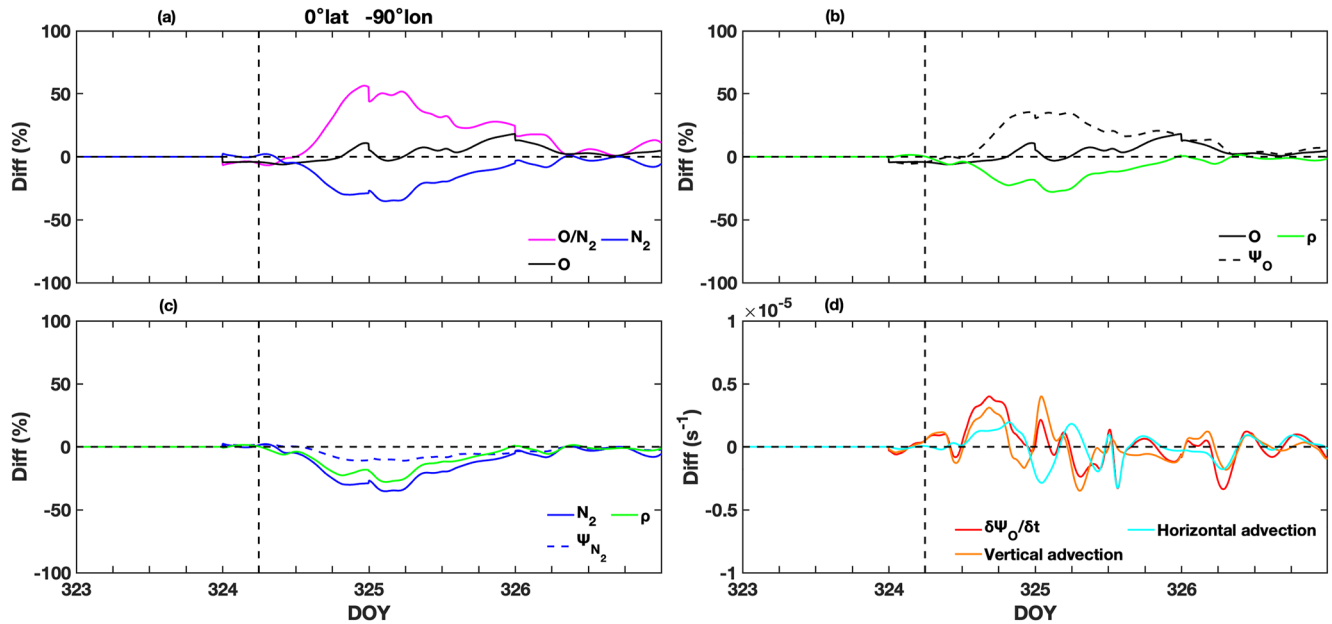
The ideal gas law:

$$P = \rho RT \quad (3)$$

$P$  is the pressure,  $R$  is gas constant, and  $T$  is the neutral temperature. Thus, in pressure coordinates, as the temperature increases (decreases) during the storm,  $\rho$  must decrease (increase) to maintain a constant pressure on a particular pressure surface.

The latitude and local time distribution of storm-quiet percentage differences of O mmr, N<sub>2</sub> mmr neutral temperature ( $T$ ) and total mass density ( $\rho$ ) at the same UTs are included in Figure 2 (fifth -eighth rows). Furthermore, a movie of the parameters in Figure 2 (Movie S1) is provided in the Supporting Information (SI) to illustrate in detail the temporal and spatial evolution of composition responses on DOY 324 and 325.

Since  $\Psi_o + \Psi_{N_2} \cong 1$  at  $\sim 160$  km, the increases of  $\Psi_o$  are approximately equivalent to the decreases of  $\Psi_{N_2}$  (Burns et al., 1989). N<sub>2</sub> is the major gas species on the  $z = -1.5$  pressure surface, thus,  $\Psi_{N_2}$  is larger relative to  $\Psi_o$ , leading to the smaller percentage changes of  $\Psi_{N_2}$  than those of  $\Psi_o$  globally shown in Figure 2. Comparing the changes of O/N<sub>2</sub> with those of O mmr and N<sub>2</sub> mmr, in the regions of O/N<sub>2</sub> depletion, O mmr decreased and N<sub>2</sub> mmr increased, which were determined mainly by the upwelling of high  $\Psi_{N_2}$  (low  $\Psi_o$ ) air from the low thermosphere at high latitudes and the horizontal advection to mid-low latitudes (Burns et al., 2006). In the regions of O/N<sub>2</sub> increases, the O mmr had an enhancement and N<sub>2</sub> mmr had a decrease, which were dependent more on the downwelling of the high  $\Psi_o$  (low  $\Psi_{N_2}$ ) air in the upper thermosphere at high latitudes and horizontal transport.  $\rho$  (last row) decreased in almost all regions on this pressure level ( $-1.5, \sim 160$  km) over the entire course of the storm, except at high latitudes on DOY 324 where it slightly increased. The ideal gas law (Equation 3) shows that  $\rho$  decreases in almost all regions were mainly due to the increases of neutral temperature shown in Figure 2. According to Equation 2,  $\rho$  reduction plus the decreases of O mmr and N<sub>2</sub> mmr can generate large decreases of O and N<sub>2</sub> number densities. By comparison,  $\rho$  reduction plus the increases of O mmr and N<sub>2</sub> mmr can cause small increases or even decreases of O and N<sub>2</sub> number densities. Therefore, in all regions of N<sub>2</sub> mmr enhancement on this pressure level, the N<sub>2</sub> mmr enhancement (0–~40%) with the  $\rho$  reduction (0–45%) resulted in the decreases of N<sub>2</sub> number density in these regions. At high latitudes of NH at 14.38 UT on DOY 324, the increases of N<sub>2</sub> number density with a maximum of  $\sim 80\%$  were caused by the enhancement of N<sub>2</sub> and  $\rho$ . In all regions of N<sub>2</sub> mmr decreases at mid-low latitudes, N<sub>2</sub> mmr decreases (0–~20%) with  $\rho$  reduction (0–40%) resulted in the larger



**Figure 3.** (a) Variations of the percentage changes in  $O/N_2$ ,  $O$ , and  $N_2$  number densities as a function of time at the location of  $0^\circ N$ ,  $90^\circ W$ ; (b) variations of  $O$  number density, atomic oxygen mass mixing ratios ( $\Psi_o$ ) and total mass density ( $\rho$ ); (c) variations of  $N_2$  number density, molecular nitrogen mass mixing ratios ( $\Psi_{N_2}$ ) and total mass density ( $\rho$ ); (d) Variations of the storm-quiet changes in the total time rate of change of  $O$  ( $\partial\Psi_o/\partial t$ ), horizontal advection and vertical advection of  $O$ .

decreases of  $N_2$  number density in these regions. Thus,  $N_2$  number density decreased almost globally on this pressure level. Similarly, the  $O$  mmr enhancement at mid-low latitudes was also weakened by the  $\rho$  reduction, which showed small changes of  $O$  number density except in the two regions with  $O$  increases of  $\sim 40\%$  and  $\sim 30\%$  during the initial and main phases of the storm. In addition, the decreases of  $O$  mmr, in conjunction with the  $\rho$  reduction, led to larger decreases of  $O$  number density on this pressure level, with a maximum magnitude of  $\sim 70\%$  at 14.38 UT on DOY 324,  $\sim 85\%$  at 19.24 UT on DOY 324, and  $\sim 80\%$  at 6.29 UT on DOY 325.

To show clearly the behavior and cause of storm-time composition changes, we selected two locations ( $0^\circ$ ,  $90^\circ W$ ;  $40^\circ S$ ,  $75^\circ E$ ) to show the variations of composition and diagnostic terms (cf. Burns et al., 2006) as a function of time on the  $z = -1.5$  ( $\sim 160$  km) pressure surface. Figure 3a shows the percentage differences of  $O/N_2$  (pink line),  $O$  (black line) and  $N_2$  (blue line) number densities from DOY 323 to 326 at the equator ( $0^\circ$ ,  $90^\circ W$ ). Storm-time  $O/N_2$  was larger than the quiet-time value for most of the times during the storm at this location;  $O$  was slightly decreased before 18 UT on DOY 324, but slightly increased after that; while  $N_2$  had a large decrease during the entire storm period. Therefore, the storm-time  $O/N_2$  enhancement on this pressure level at this location depend mainly on the  $N_2$  decreases. The causes of  $O$  changes are shown in Figure 3b: the storm-time increases of  $\Psi_o$  (black dashed line) were offset by the decreases of  $\rho$  (green line). Figure 3c shows that  $\Psi_{N_2}$  had a small decrease on this pressure level. The tendency of  $N_2$  percentage changes was basically the same as that of  $\rho$  changes. Figure 3d shows the changes in the total time rate of change of  $O$  ( $\partial\Psi_o/\partial t$ ), and horizontal and vertical advection of  $O$ . The comparison of the morphology and magnitude between the horizontal (cyan line) and vertical (yellow line) advection with  $\partial\Psi_o/\partial t$  (red line) shows that both the vertical and horizontal advection were crucial to the change of  $\Psi_o$  at this location.

Figure 4 is the same format as Figure 3, but at the location of  $40^\circ S$ ,  $75^\circ E$ . Figure 4d shows that the storm-time responses at this location were mainly driven by the horizontal advection. The  $O/N_2$  increase at 0 UT on DOY 324 was the day-to-day variation mentioned before. The second  $O/N_2$  increase occurred from  $\sim 12$  UT to 18 UT on DOY 324. Obviously, this  $O/N_2$  increase was the result of the downwelling at high latitudes and then propagated to this location by the horizontal advection (See Movie S1). Movie S1 shows that the  $O/N_2$  increase near this location changed to large decreases along as the storm progressed. Figure 4a shows that  $O$  and  $N_2$  both played a role in this  $O/N_2$  enhancement.  $O/N_2$  storm-time decreases, such as that occurred from  $\sim 18$  UT on DOY 324 to 12 UT on DOY 325 (Figure 4a), were primarily caused by the large  $O$  reduction. Figure 4b shows that the  $O$  changes depended more on the  $\Psi_o$  changes compared to those of  $\rho$ .  $\Psi_{N_2}$  changed a little on this pressure level, and the tendency of  $N_2$  changes was almost the same as that of  $\rho$  changes (Figure 4c).

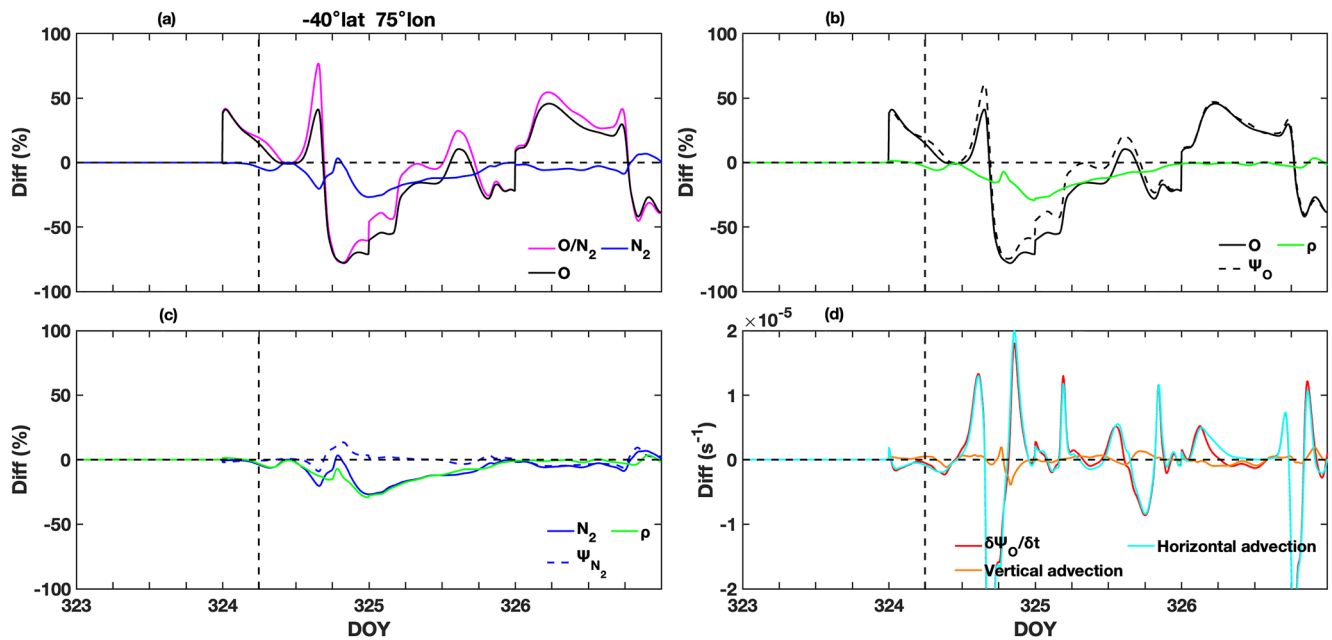
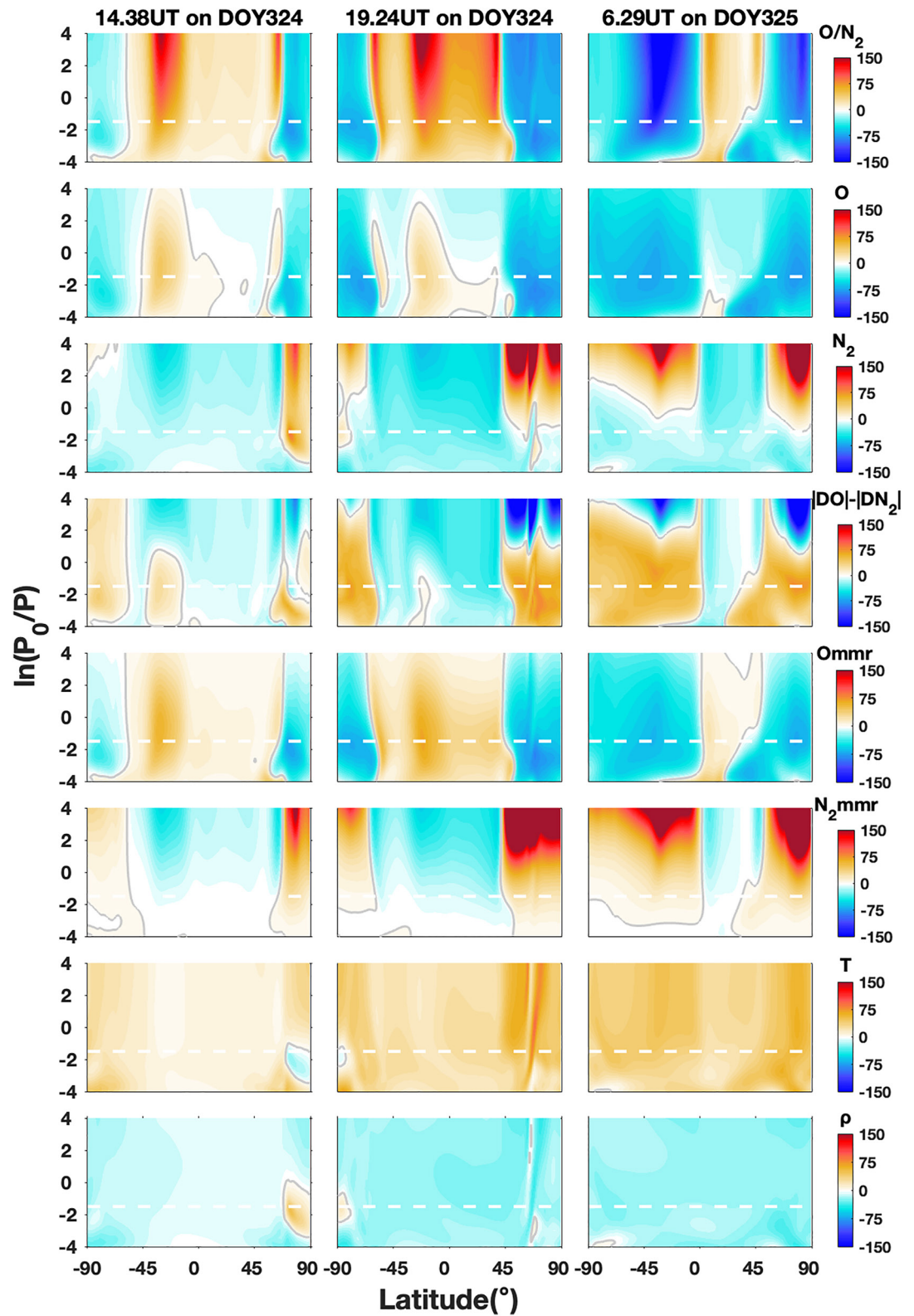


Figure 4. Same as Figure 3, but at the location of 40°S, 75°E.

Furthermore, Figure S1 in Supporting Information S1 shows the total time rate of change of  $N_2$  ( $\partial\Psi_{N_2}/\partial t$ ), and horizontal and vertical advection of  $N_2$ . Similar to O, horizontal advection and vertical advection dominated the storm-induced  $N_2$  changes at the location of 0°, 90°W. At the location of 40°S, 75°E, storm-time  $N_2$  responses were mainly driven by the horizontal advection. Thus, the changes of O and  $N_2$  number densities can be explained by the changes of their mass mixing ratio and  $\rho$ . The storm-induced changes of  $\Psi_O$  and  $\Psi_{N_2}$  depend primarily on the upwelling and downwelling of air and horizontal advection. The global  $\rho$  reduction during the storm is due to the storm-induced temperature enhancement.

### 3.3. Changes in the Vertical Direction

Figure 5 shows the pressure surface-latitude distributions of storm-quiet percentage changes in  $O/N_2$ , O,  $N_2$  number density and the differences of absolute value of O and  $N_2$  changes, and the percentage changes of O mmmr,  $N_2$  mmmr, neutral temperature and total mass density at the longitude of 0° at the same UTs as in Figure 2. The vertical axis is in pressure coordinates from  $z = -4$  (~120 km) to  $z = 4$  (~450 km). Table in the SI show the different pressure levels and their corresponding approximate altitudes. Additionally, Figure S2 in Supporting Information S1 shows the changes of these parameters in altitude coordinate for the quantitative presentation of the effects from the thermal expansion. Movie S2 shows the temporal evolution of the parameters in Figure 5 on DOY 324 and 325. Figure 5 indicates that the behaviors of  $O/N_2$  perturbations on different pressure levels were similar above the  $z = \sim -1.5$  (~180 km) pressure level. As is mentioned in the Introduction, the storm-time electron density changes are more relevant to the local  $O/N_2$  changes at a given altitude, not the  $\sum O/N_2$ . However, the correlation between the peak electron density in the F layer and  $\sum O/N_2$  have been investigated by many studies based on the thermospheric and ionospheric observations (Kil et al., 2011b; Lee et al., 2013; Strickland et al., 2001). O and  $N_2$  column densities in the middle thermosphere (~140–180 km) make a major contribution to  $\sum O/N_2$ , due to the exponential decay of O and  $N_2$  number densities with altitude (Strickland et al., 1995; Yu et al., 2020, 2021a; Yue et al., 2019). Therefore, the storm-induced electron density variations in the ionosphere  $F_2$  region are sometimes closely correlated with the neutral composition perturbation in the middle thermosphere, which can be explained by the similar perturbation morphology of  $O/N_2$  at different altitudes as shown in Figure 5. Similarly, Lei et al. (2010) emphasized the high correlation between  $O/N_2$  on the  $z = 3$  (~400 km) pressure surface and  $\sum O/N_2$ . In the middle and low thermosphere below ~180 km, the  $O/N_2$  perturbations were highly dependent on the altitude, and related to the storm evolution. The storm-induced perturbations of O and  $N_2$  number densities had significant latitude dependence at all pressure levels, which were also changing as the storm progressed.



**Figure 5.** (top to bottom) The percentage changes in  $O/N_2$ ,  $O$ ,  $N_2$  number density, the differences of absolute value of  $O$  and  $N_2$  percentage changes,  $O$  mass mixing ratios ( $O$  mmr),  $N_2$  mass mixing ratios ( $N_2$  mmr), temperature ( $T$ ) and total mass density ( $\rho$ ) in pressure coordinates at the longitude of  $0^\circ$  at three UTs (left to right). In each panel the gray curves indicate the zero value, and the white dashed line is the  $z = -1.5$  pressure surface.

We first analyze the storm-time perturbation behaviors of O mnr and N<sub>2</sub> mnr shown in Figure 5. In the storm initial phase (14.38 UT), weak upwelling at high latitudes occurs as a result of the increased temperature, and high  $\Psi_{N_2}$  (low  $\Psi_O$ ) air in the low thermosphere was transported to the upper thermosphere. Thus, a small reduction of O mnr (0~70%) and an enhancement of N<sub>2</sub> mnr (0~180%) occurred at all pressure levels of the high latitudes. At the same time, the downwelling at lower latitudes leads to the opposite perturbation behaviors of O mnr (increase of 0~60%) and N<sub>2</sub> mnr (decrease of 0~60%). The temperature differences in the latitudinal direction were also set up, leading to an equatorward pressure gradient, which drove equatorward horizontal winds. The equatorward flow carried the composition changes to lower latitudes. As the storm proceeded, in the storm main phase (19.24 UT), upward and downward winds both became much stronger, which resulted in considerably larger composition changes. The temperature differences in the latitudinal direction were also large, resulting in a strong equatorward flow. Thus, the reduction of O mnr (0~85%) and the increases of N<sub>2</sub> mnr (0~850%) at high latitudes were transported to a wider latitude range during the main phase of the storm, which is the result of horizontal transport effects (Burns et al., 2006). The latitudinal and altitudinal dependency of composition perturbations is partly determined by the magnitude differences of horizontal wind perturbations at different altitudes and latitudes during the storm. During the recovery phase of the storm (6.29 UT on DOY 325), O mnr reduction of 0~65% (N<sub>2</sub> mnr enhancement of 0~550%) in the SH was transported to the equator. While the O mnr reduction (0~70%) and N<sub>2</sub> mnr enhancement (0~750%) extended to ~45° N above the  $z = -1$  pressure level in the NH, and the lowest latitude of O mnr reduction changed gradually to ~20° N at  $z = -4$  pressure level at this longitude. Additionally, the O mnr changes (increase and decrease) had a maximum along with the altitude over the entire storm period, mainly on the  $z = -1.5$  pressure surface. However, N<sub>2</sub> mnr changes increased with the increase of altitude.

Figure 5 shows that the total mass density (last row) decreased almost at all pressure levels except in some regions at the high latitudes of NH at 14.38 UT where it had an increase. This should be also explained by the temperature variations in pressure coordinates. Thus, the decreased total mass density, in conjunction with the changes of O mnr and N<sub>2</sub> mnr, explained the perturbation behaviors of O and N<sub>2</sub> number densities. In the storm initial phase (14.38 UT), small N<sub>2</sub> mnr increases (<~30%) at the high latitudes of the SH plus the  $\rho$  reduction (0~50%) resulted in the decreases of N<sub>2</sub> number density in these regions. At high latitudes of the NH, however, N<sub>2</sub> increased with a maximal magnitude of ~75%. During the main and recovery phases of the storm, N<sub>2</sub> decreased at mid-high latitudes in the middle thermosphere due to the offset between the  $\rho$  reduction and the small N<sub>2</sub> mnr increases. Whereas at mid-high latitudes in the middle and upper thermosphere (above  $z = -1$  pressure level), N<sub>2</sub> has an enhancement, and the enhancement increased with altitude, reaching more than 700% at mid-high pressure levels. Similarly,  $\rho$  reduction can offset the enhancement of O mnr at mid-low latitudes. Thus, the O number density had a small enhancement (0~30%) or even a small decrease of less than ~20% in the region of O mnr enhancement during the entire storm.  $\rho$  reduction contributes to the decreases of O mnr at mid-high latitudes and N<sub>2</sub> mnr at mid-low latitudes at all pressure levels. Therefore, in these regions of O mnr and N<sub>2</sub> mnr decreases, O number density had a decrease of 0~85%, and N<sub>2</sub> number density had a decrease of 0~45% during the storm. The global decreases of N<sub>2</sub> number density were observed in the middle thermosphere, which were deviated from the previous cognition about the storm-time N<sub>2</sub> increases at high latitudes in altitudes coordinates.

Now we analyze the relative contributions of the storm-time perturbations of O, N<sub>2</sub> number density to O/N<sub>2</sub> variations. The fourth row shows the main reasons of O/N<sub>2</sub> perturbations at different latitudes and pressure levels. In the regions of O/N<sub>2</sub> enhancement (cf. first row, Figure 5), mostly at middle and low latitudes, the negative values of the absolute difference of O and N<sub>2</sub> percentage changes (0~ -50%) indicate that the percentage changes of O (decrease or increase) are smaller than those of N<sub>2</sub>. Thus, O/N<sub>2</sub> enhancement at middle and low latitudes was more related to the N<sub>2</sub> decrease at all pressure surfaces during the entire storm period. It should be noted that there is a special region in the initial and main phases of the storm, where the absolute difference of O and N<sub>2</sub> percentage changes is positive (0~25%). At 14.38 UT on DOY 324, the region was located at ~45° S~10° S between  $z = -4$ ~ $-1$  pressure levels, and it shrunk to ~30° S~10° S latitude range from  $z = -4$  to  $-1$  pressure levels at 19.24 UT on DOY 324. The positive values indicate the important effects of O to O/N<sub>2</sub> increases in this region. As aforementioned in Section 3.2, the composition perturbations in this region were mainly driven by the horizontal advection, corresponding to the large O increases in the ~0°~45° S latitudes at 14.38 UT and 19.24 UT on DOY 324 in Figure 2. Movie S2 shows the evolution of the responses more clearly.

The main cause of O/N<sub>2</sub> decreases depends on altitude. At 14.38 UT on DOY 324, the absolute differences of O and N<sub>2</sub> percentage changes are positive with a magnitude of 0~40% at all pressure levels of SH in the regions

of  $O/N_2$  decreases (cf. first row, Figure 5). O decrease plays a vital role in the  $O/N_2$  decreases in these regions. However, negative values of the absolute difference (0 ~ -100%) occurred above  $z = \sim 0$  pressure level in the NH in the regions of  $O/N_2$  depletion, which indicates that  $N_2$  enhancement can be significant in the upper thermosphere. At 19.24 UT on DOY 324, at mid-high latitudes,  $N_2$  increases have a larger contribution to  $O/N_2$  decreases above the  $z = \sim 3$  pressure level in the SH, while above the  $z = \sim 1$  pressure level ( $\sim 300$  km) in the NH. Therefore, there exist transition heights of the contributions from O and  $N_2$  number densities to  $O/N_2$  decreases during the storm. Above the transition heights, the storm-time  $O/N_2$  depletion is more related to the large  $N_2$  enhancement. At 6.29 UT on DOY 325,  $O/N_2$  decreases in the SH were transported to the equator. The transition heights were at  $z = 1.5$  pressure level at  $\sim 30^\circ$  S, and increased to both sides in the latitude range of  $O/N_2$  depletion in the SH. In the NH,  $O/N_2$  decreases extended to  $\sim 45^\circ$  N above the  $z = \sim -1$  pressure level. The transition heights were at about  $z = 0.5$  pressure level at  $\sim 80^\circ$  N, and also increased to both sides in the latitude range of  $O/N_2$  depletion in the NH. Therefore, the contributions from O and  $N_2$  number densities to  $O/N_2$  decreases on different pressure levels have altitude and latitude differences. Storm-induced  $O/N_2$  depletion is more related to the O reduction at lower thermosphere (below the transition heights), but depend on the  $N_2$  enhancement in the upper thermosphere (above the transition heights).

#### 4. Conclusion

A first principles model of the coupled thermosphere and ionosphere (TIEGCM) was used to investigate the vertical variations of thermospheric  $O/N_2$  at different pressure levels and its dependence on the O and  $N_2$  perturbations during the November 20 and 21, 2003 superstorm event. The main conclusions are:

1. In the middle and low thermosphere of below  $\sim 300$  km, the storm-time  $O/N_2$  depletion is primarily associated with a large reduction of O number density. In the upper thermosphere of above  $\sim 300$  km,  $N_2$  enhancement plays an important role in the  $O/N_2$  decreases.
2. The contributions of O and  $N_2$  perturbations to  $O/N_2$  enhancement are similar at all pressure levels. The storm-induced  $O/N_2$  enhancement was mainly related to the large  $N_2$  decreases, except in some regions where O and  $N_2$  changes are both important for  $O/N_2$  changes.
3. In the regions of  $O/N_2$  decreases, O mnr decreased and  $N_2$  mnr increased at all pressure levels, driven by the upwelling of high  $\Psi_{N_2}$  (low  $\Psi_o$ ) air from the lower thermosphere and horizontal advection. In the regions of  $O/N_2$  increases, O mnr enhanced and  $N_2$  mnr decreased, driven by both the downwelling of low  $\Psi_{N_2}$  (high  $\Psi_o$ ) air from the upper thermosphere and horizontal transport.
4. The total mass density at constant pressure levels decreased almost globally over the entire storm period due to temperature increases. The storm-induced perturbations of O and  $N_2$  number densities can be explained by the superposition of changes of their mass mixing ratio and total mass density.

#### Data Availability Statement

AE, Dst,  $K_p$ ,  $B_y$  and  $B_z$  indices are from [https://cdaweb.gsfc.nasa.gov/cdaweb/sp\\_phys/](https://cdaweb.gsfc.nasa.gov/cdaweb/sp_phys/). The TIEGCM simulation results are available at <https://doi.org/10.5281/zenodo.7479451> (Yu, 2022).

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