Reply to Referee 1

We are grateful to the referee for the encouraging comments and careful revisions which helped to improve the quality of our paper. In the following we quoted each review question in the square brackets and added our response after each paragraph.

[1. There is no doubt that the intrusion of O3-rich air from the UTLT region is critical to occurrence of the O3 episode. However, it is not sufficient to draw the conclusion that the photochemical production of O3 is negligible if the NO2 concentration is not changed. As we know, the weather is characterized by the clear sky, strong solar radiation, weak wind, and stable atmospheric boundary layer when a typhoon is about 600 to 1000 km away. All these are the favorable conditions for photochemical production of O3.]

Reply 1: The comments are great appreciated. We agree with the reviewer and have accordingly added the following discussion at the end of second paragraph in Section 3:

"The weather over the XQR region was characterized by the clear sky, strong solar radiation, weak wind, and stable atmospheric boundary layer when TC is about 600 to 1000 km away during the O_3 episode of 12-14 June (Fig. 4). All these are the favorable conditions for photochemical production of O_3 , which is confirmed by the diurnal variation of O_3 during the episode (Fig. 3d), However, a comparison of diurnal O_3 changes in June 2014 and during the O_3 episode (Fig. 3d) clearly presents the anomalies in the diurnal O_3 variation over June 12-14, suggesting a less contribution of the local photochemical O_3 production to the peak O_3 . "

[2. Figure 3&4 need to be organized, time series of all the related variables during the episode should be shown in one figure (in different rows) for an easy comparison.]

Reply 2: Thank the reviewer for this suggestion. Figures 3 and 4 present the temporal variations in atmospheric tracers and meteorological conditions respectively. For an easy comparison in these the temporal variations, we have added the red rectangular columns marking the period of surface O3 event o June 12-14, 2014 over XQR in Figures 3 and 4.

[3. Figure 6. I am not quite sure about the data points in the figure, does it include both daytime data and nighttime data? If both daytime and nighttime are included, I am not sure

what the figure really means. Note that in the daytime, more primary pollutants may lead to O3 production, while in nighttime more primary pollutants (e.g., NOx) lead to O3 titration.]

Reply 3: Thank the referee for the kind suggestions. We agree the referee's opinions of different effects of primary pollutants on O_3 changes in daytime and nighttime. In our study, the correlations between O_3 and CO are used to identify the contributions of anthropogenic sources and UTLS downward transport to the tropospheric O_3 changes in the different periods. Furthermore, an O_3 episode with high nighttime O_3 was observed before typhoon landing over 12-14 June, Therefore, the correlation analysis include both daytime data and nighttime data in Fig. 6.

[4. It is better to indicate the hurricane track in Figure 2 and indicate during which period the surface 03 increased.]

Reply 4: Following the Referee's suggestion, we have added the typhoon track in Figure 2c indicating the typhoon locations during the different periods.

[5. Line 27, page 24626, change "by the downward O3 from" to "due to the downward O3 transport from"]

Reply 5: Thanks a lot. In the revised version, we modified it followed the suggestion.

[6. Line 20, page 24628, "abruptly" may not be appropriate.]

Reply 6: Thanks for the suggestion. We have revised "abruptly" to "obviously" in revised version.

[7. LN7-8, page 24629, "Tropospheric O3 is produced". this sentence is repetitive.]

Reply 7: Thanks for the suggestion. It has been corrected.

[8. LN14-15, page 24629, "Therefore" is not appropriate/robust here. Photochemical production depends not only on NOx level, but also on other meteorological factors, e.g., radiation, temperature.]

Reply 8: We delete the "Therefore" in the revised manuscript.

[9. LN19, page 24629, "As we know", why don't show it in a figure?]

Reply 9: Thanks for the suggestion. We have modified it with the following sentences: "The weather over the XQR region was characterized by the clear sky, strong solar radiation, weak wind, and stable atmospheric boundary layer when TC is about 600 to 1000 km away during the O₃ episode of 12-14 June (Fig. 4)."

[10. LN21, page 24630, "strong downdrafts", how strong is "strong"?]

Reply 10: Thanks for the comment. In the revised version, we have added the description of "strong downdrafts" with following sentence: "The well-organized deep and strong downdrafts occurred over XQR during this episode before the typhoon landfall with the subsiding velocity exceeding 20 Pa s⁻¹at 14:00 and 20:00 in June 13."

[11. LN 28, page 24631, "the reaction of CO with OH quickly forms.", I thought the lifetime of CO is quite long.]

Reply 11: We agree with referee and delete the "quickly" in the revised manuscript.

[12. LN10, page 24632, "an exceptionally high O3". Not really that high.]

Reply 12: Thanks for the comment. The word "exceptionally" really overrates the O3 levels during this episode. We have already deleted "exceptionally" in the revised manuscript.

Reply to Referee 2

We are grateful to the referee for the encouraging comments and careful revisions which helped to improve the quality of our paper. In the following we quoted each review question in the square brackets and added our response after each paragraph.

[1. My biggest concern is about tracking the ozone source using O3/CO correlations. Previous studies showed that positive and negative correlations reveal difference ozone

production/transport mechanism in troposphere. However, this needs some other factor such as weather and air pollution conditions to be excluded. As to this paper, ozone production might be halted under cloudy conditions on June 14, 2014 just before the typhoon's landing. However, CO is continuously emitted. As a result, there may be a negative O3/CO correlation with high CO abundances. I think this scenario should be cleared before linking this event with STE, though the weather condition might favorite a descent from the upper troposphere. Fig 5 shows descent at 20:00h June 13 and ascent. However, it is not clear that was the case for the whole period 12:00h June 13 - 12h June 14 (the period for Fig 6b) because the last panel in Fig 5 shows the ascent at 20:00h June 15.]

Reply 1: We thank the reviewer for the great suggestions. We agree with the reviewer. The O3 production from photochemical reaction might be less in cloudy days comparing to sunny days. In our study, the correlations between O_3 and CO are used to identify the contributions of anthropogenic sources and UTLS downward transport to the tropospheric O_3 changes in the different periods. Furthermore, an O_3 episode with high nighttime O_3 was observed before typhoon landing over 12-14 June, Therefore, the correlation analysis include the O_3 episode in Fig. 6.

[2. Page 24627: Line 118, remove the word "stratospheric".]

Reply 2: Following the reviewer's suggestion, we modified it in the revised version.

[3. Page 24628: Line 21-25, this sentence needs to be re-worded.]

Reply 3: Thanks for the suggestions. We have re-worded it with the following sentences in the revised manuscript:

"By using the hourly O_3 measurement data over XQR, the normal and anomalous patterns of diurnal O_3 changes could be represented by the surface O_3 averages over June 2014 excluding 12–14 June and over 12–14 June 2014 respectively (Fig. 3d)."

[Page 24633: Line 3-4, what are the "implications"? The authors should specify it even too many details are not necessary.]

Reply 4: Followed the sentence, we have added "Tropical cyclones, as an important STE mechanism, could exert an enormous impact on air mass and energy transports in the troposphere, as well as redistribution of tropospheric ozone." in the revised manuscript.

Why does surface ozone peak before a typhoon landing in

2 southeast China?

3

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2

Key Points

- An O₃ episode with high nighttime O₃ was observed before typhoon landing
- The subsiding branches of TC circulation were identified to enhance surface O₃
- The STE of O₃ driven by the large scale TC can threaten to ambient air quality

6

7

Abstract

- 8 A high O₃ episode with the large increases in surface ozone by 21-42 ppbv and the nocturnal
- 9 surface O₃ levels exceeding 70 ppbv was observed in the region between Xiamen and
- Quanzhou over the southeastern coast of China during June 12-14, 2014, before Typhoon
- Hagibis landing. Variations in the surface O₃, NO₂, CO and meteorology during Typhoon
- 12 Hagibis event clearly suggest a substantial impact of the peripheral downdrafts in the large
- scale typhoon circulation on such an O₃ episode with excluding the contributions of
- photochemical production and the horizontal transport. The influence of vertical O₃ transport
- 15 from the upper troposphere and lower stratosphere (UTLS) region on high surface O₃ levels is
- further confirmed by a negative correlation between surface O₃ and CO concentrations as well
- as dry surface air observed during the O₃ episode. This study provides observational evidence
- of typhoon-driven intrusion of O₃ from the UTLS region to surface air, revealing a significant
- 19 effect of such a process of stratosphere-troposphere exchange (STE) of O₃ on tropospheric O₃
- 20 and ambient air quality.
- 21 **Key words:** typhoon, ozone episode, vertical transport, stratosphere-troposphere exchange

2223

1 Introduction

- 24 Tropospheric O₃, as an important chemical species with the effects of oxidation, toxicity and
- 25 greenhouse gas on climate and environment, is generated through a series of complex
- 26 photochemical reactions related to oxides of nitrogen (NO_x) and volatile organic compounds
- 27 (VOC) under strong solar radiation. Both strong local photochemical production and
- atmospheric transport processes can lead to high surface O₃ concentrations (Jacob, 1999).
- 29 Weather condition can profoundly influence tropospheric O₃ levels through physical and

- 1 chemical processes and their interactions that modulate O₃ and its precursors (Huang et al.,
- 2 2005; Xue et al., 2014). The variation of tropospheric O₃ is largely influenced by the STE of
- 3 air mass and chemical species (Holton et al., 1995; Tang et al., 2011; Hsu and Prather, 2014).

- 5 A tropical cyclone (TC), as a large scale weather system with strong convection, is referred to
- 6 as a typhoon over the Western Pacific or a hurricane over the Northern Atlantic. A typical TC
- 7 can span a large radius of 100-2000 km with the vertical circulation of strong convection
- 8 extending into the UTLS region at heights of 10-18 km (Emanuel, 1986). A three-dimensional
- 9 TC circulation consists of the rotational air flow in the horizontal direction and the
- 10 in-up-out-down overturning flow in the vertical direction, along which air mass near the
- 11 surface can rise into thunderstorm clouds, outflowing at high levels in the UTLS and
- subsiding in the periphery. As an important STE mechanism, the vertical TC circulation with
- 13 internal updrafts and peripheral downdrafts between the surface and the UTLS region exerts
- an enormous impact on air mass and energy transports in the troposphere (Baray et al., 1998;
- Fadnavis et al., 2011), as well as redistribution of tropospheric O₃ (Baray et al., 1999).

16

- 17 Air intrusions from the stratosphere to the troposphere were speculated to increase O₃
- concentrations in the upper troposphere during a TC event (Bellevue et al., 2007). The uplift
- 19 flows of TC also transport O₃ from the surface to the middle and upper troposphere (Fadnavis
- et al., 2011). Under the influence of frequent typhoon activities, O₃ episodes occurred over
- 21 coastal areas in southeast China (Feng et al., 2007; Wu et al., 2013). The stagnant
- 22 meteorological conditions with strong subsidence and stable stratification in the boundary
- layer resulted in pollutant accumulations with high O_3 before typhoon landings over southeast
- 24 China (Feng et al., 2007). The peripheral O₃ was regionally transported by strong horizontal
- 25 typhoon winds (Huang et al., 2006).

- 27 Convection and orographic forcing can be important for the STE and the modification of trace
- 28 gases between the boundary layer and the free troposphere (Lelieveld and Crutzen, 1994;
- 29 Donnell et al., 2001; Weber and Prevot, 2002; Ding et al., 2009). O₃-rich air aloft could be
- 30 transported downward to the surface, when the cold front passage or nocturnal residual layer

"leaky" occurred (Hu et al., 2013a, 2013b). The near-surface O₃ levels abruptly increased <u>due</u> to the downward O₃ transport fromby the downward O₃ from the free troposphere by tropical convections, enhancing O₃ levels in the boundary layer by as much as 20 to 30 ppbv (Betts et al. 2002; Sahu and Lal 2006; Grant et al. 2008). A recent modeling study (Hu et al., 2010) estimated that the downward transport resulted in a 39% increase in the O₃ burden within the lower atmosphere (<2 km) during a deep moist convection event over West Africa in August 2006. These studies on downdrafts of O₃ to the surface level are mostly focused on the

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8 mesoscale convections in the tropics. The extent to which these UTLS ozone enhancements

9 reach the surface is poorly characterized.

Redistribution of tropospheric O₃ by the TC circulation has been studied from the perspectives of the STE of O₃, strong horizontal advection, and the stagnant meteorology for O₃ accumulations in the boundary layer. In this study, we report a new finding on the O₃-rich air downdrafts from the UTLS region to the surface driven by vertical typhoon circulation, as the deep stratospheric intrusions elevating western US of surface O₃ to unhealthy levels can be classified as "exceptional events" (Lin et al., 2015). We investigate the O₃ variation during a TC event of Typhoon Hagibis over northwest Pacific on the basis of observations of the surface air pollutants and meteorology in Xiamen and Quanzhou region (XQR) over the southeastern coast of China (Fig. 1) in June 2014. This study presents observational evidence of a surface O₃ episode caused by downward transport of O₃ in the subsiding branches of vertical TC circulation. this finding may shed some light on the function of downward O₃ transport from the UTLS/stratospheric regions in modulating O₃ in the lower troposphere with implications of the STE on air quality and climate changes.

2 Data and Observation

The XQR area, a prefecture of Fujian Province, located in the western coast of Taiwan Strait, southeast China (Fig. 1). The air quality data (http://air.epmap.org/), including surface concentrations of O₃, nitrogen dioxide (NO₂) and carbon monoxide (CO), were measured at 8 environmental monitoring stations over XQR in June, 2014. The surface observations of wind, air temperature, air pressure and relative humidity at the observatory of Xiamen (24.48°N, 118.07°E) were collected for meteorological analysis during Typhoon Hagibis in June 2014.

- The FNL meteorological data in a horizontal resolution of 1 x1 with 27 vertical levels from
- 2 NCEP (National Centers for Environmental Prediction, USA) are used to describe the
- 3 circulations of Typhoon Hagibis.

- 5 Typhoon Hagibis, as a summertime TC over the northwest Pacific, was intensified into a
- strong tropical storm over the South China Sea at Dongsha islands (116.8°E, 20.6°N) and then
- 7 gradually pushed northwards up the southeastern coast of China. Typhoon Hagibis made
- 8 landfall in Shantou, a coastal site of Guangdong Province, south of XQR, at 16:50 June 15
- 9 (local time, same for hereinafter) with the maximum sustained winds of 23 m s⁻¹. Figures
- 2a-2c show the distributions of sea-level pressure and near-surface wind fields over the region
- from southeast China to northwest Pacific at 14:00 June 13, 20:00 June 13 and 20:00 June 15,
- 12 2014 respectively, before and after the typhoon landing in the southeastern coast of China.

13

- 14 The hourly surface O₃ concentrations over XQR during Typhoon Hagibis are shown in Figure
- 3a with a noticeable anomaly in O₃ concentrations before and after the typhoon landfall. XQR
- 16 was situated in the typhoon periphery when Typhoon Hagibis was located in South China Sea
- during June 12-14, 2014 (Figs. 2a and 2b). A high O₃ episode occurred from the noon of June
- 18 12 to the afternoon of June 14. In particular, the nocturnal surface O₃ concentrations exceeded
- 19 70 ppbv from June 13 to 14, 2014 (Fig. 3c). The 8-hour averaged surface O₃ concentrations of
- 20 80 ppbv at Huli and Xidong (sites 5 and 6 in Fig. 1) in XQR reached the "hazardous" O₃ level
- 21 of the Chinese national standards for ambient air quality. The surface O₃ obviouslyabruptly
- 22 decreased over XQR when Typhoon Hagibis was closer to the landfall in southeast China on
- 23 June 15, 2014 (Fig. 2c). By using the hourly O₃ measurement data over XQR, the normal and
- 24 anomalous patterns of diurnal O₃ changes could be represented by the surface O₃ averages
- over June 2014 excluding 12–14 June and over 12–14 June 2014 respectively (Fig. 3d). By
- 26 using the hourly O₃ measurement data over XQR, the normal and anomalous patterns of
- 27 averaged diurnal O₂ changes respectively in June 2014 excepting 12 14 June and over 12 14
- 28 June 2014 could be represented (Fig. 3d). By using the hourly O₃ measurement data over XQR,
- 29 the normal and anomalous patterns of diurnal O₃ changes in June 2014 and the O₃ episode
- 30 could be represented with the surface O₃ concentrations averaged respectively in June
- 31 excepting June 12-14 and over June 12-14, 2014 (Fig. 3d). It is shown in Figure 3d that the

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- 1 normal surface O₃ levels over XQR in June 2014 shifted diurnally from 17 ppbv at 2:00 to 52
- 2 ppbv at 14:00 with a daily O₃ mean of about 30 ppbv, while the anomalously high surface O₃
- 3 levels during the O₃ episode varied between nighttime 51 ppbv and daytime 70 ppbv with an
- 4 O₃ mean of about 57 ppbv. Comparing to the normal O₃ levels in June 2014, the averaged
- 5 enhancements of surface O₃ by about 21 ppbv in daytime and up to 42 ppbv in nighttime over
- 6 XQR are estimated for the O₃ episode before Typhoon Hagibis landing.

3 Analysis and Discussion

- 9 The surface O₃ variation is complex, resulted from interactions of chemical production and
- dynamic transport on different scales (Jacob, 1999). In the following we examine this case of
- surface O₃ peak before a typhoon landing in southeast China from chemical production,
- 12 horizontal advection and vertical transport.

13

- 14 Tropospheric O₃ is <u>formedproduced</u> through a series of complex photochemical reactions of
- 15 NO_x and VOC under strong solar radiation. The O₃ concentrations in suburban and rural areas
- are usually most sensitive to NO_x variations (Chameides et al., 1992; Duncan and Chameides,
- 17 1998). Notably, the surface NO_2 levels kept around 10 ppbv during the O_3 episode from June
- 18 12 to 14, almost the same as normal NO₂ levels during non-polluted days (Figs. 3b and 3c). In
- 19 particularly high O₃ levels anomalously persisted in the night without photochemical reaction.
- 20 Therefore, pPhotochemical production could not be speculated to determine the high O₃
- 21 episode. Furthermore, any obvious increases in surface air temperature were not observed for
- 22 strong photochemical reactions for such high O₃ production during the episode of June 12-14
- 23 in XQR (Fig. 4a), since air temperature could represent the solar radiation conditions during
- 24 summertime. The weather over the XQR region was characterized by the clear sky, strong
- 25 solar radiation, weak wind, and stable atmospheric boundary layer when TC is about 600 to
- 26 1000 km away during the O₃ episode of 12-14 June (Fig. 4). As we know, the weather is
- 27 characterized by the clear sky, strong solar radiation, weak wind, and stable atmospheric
- 28 boundary layer when TC is about 600 to 1000 km away. All these are the favorable conditions
- 29 for photochemical production of O₃, which is confirmed by the diurnal variation of O₃ during
- 30 the episode (Fig, 3d), However, a comparison of diurnal O₃ changes in June 2014 and during
- the O_3 episode (Fig. 3d) clearly presents the anomalies in the diurnal O_3 variation over June

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1 12-14, suggesting a less contribution of the local photochemical O₃ production to the peak O₃.

During June 12-14, weak easterly winds over XQR (Fig. 2a, Fig. 4b) were observed to be unfavorable for horizontal transport of O₃ and its precursors. The easterly wind could even carry clean air from the Pacific Ocean to XQR. Moreover, the daily change of near-surface air mass divergence over XQR clearly presented a shift of the negative to positive values for convergence and divergence conditions during normal and high O₃ periods (Fig. 3b). The near-surface air mass divergence (positive values in divergence in Fig. 4b) in association with a high surface air pressure (Fig. 4c) over XQR suppressed the advection import O₃ and its precursors towards XQR during the O₃ episode of June 12-14, 2014. The meteorological conditions of easterly clean air from ocean and near-surface air divergence over XQR were unfavorable to horizontal transport of air pollutants to XQR during the O_3 episode. Therefore, the surface O₃ peak of June 12-14 before the typhoon landing was unlikely caused by horizontal advection or transport of O_3 and its precursors.

Figures 5 presents the cross sections of vertical velocity along the lines from the typhoon center to XQR (as shown in Fig. 2 with the black solid lines) at 14:00 and 20:00 June 13, as well as 20:00 June 15, 2014 respectively. In accompany with the strong rising motions from the surface up to the UTLS around 100 hPa near the typhoon center (Figs. 5a and 5b), the subsiding branches of vertical typhoon circulation were located over XQR in the northeastern periphery of Typhoon Hagibis at 14:00 and 20:00 June 13, 2014 (Figs. 2a and 5a, Figs. 2b and 5b). A typical structure of TC circulation with the in-up-out-down overturning flows in the vertical direction built up the internal updrafts and peripheral downdrafts for air mass exchange between the surface level and the UTLS region (Figs. 5a-5b). The well-organized deep and strong downdrafts occurred over XQR (24°N, 118°E) during this episode before the typhoon landfall, the downward flow has exceeded 20 Pa/s at 14:00 and 20:00 in June 13. As Typhoon Hagibis approached and landed the coast in southeast China (Fig. 2), the downdrafts were changed to the updrafts over XQR on June 15 (Fig. 5c), and the surface O₃ concentrations dropped to the normal levels over XQR (Fig. 3a).

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A climatological pattern of vertical O₃ distribution presents the uniquely elevated O₃ 1 concentrations in the UTLS region (Liu et al., 2013). The large scale convections of Typhoon 2 Hagibis were fully developed and well organized with strong uplifts reaching to the UTLS 3 around 100hPa and consecutively downward flows to the surface level over XQR (Figs. 4 5a-5b), which could efficiently deliver O₃-rich air from the UTLS region to the surface 5 leading to the surface O₃ enhancement by about 27 ppbv in daytime and up to 40 ppbv in 6 7 nighttime observed over XQR during June 12-14 (Figs. 3c-3d). Furthermore, low relative humidity and high air pressure on the XQR surface during June 12-14 (Figs. 4c and 4d) add 8 9 evidences for the strong downward transport of O₃ in the subsiding branches of TC with dry 10 air mass of the UTLS region affecting the surface air, given that surface relative humidity dropped sharply (Fig. 4d) and air temperature decreased slightly (Fig. 4a) over XQR during 11 June 12-14. Therefore, it is the downdrafts of O3-rich air from the UTLS that played a 12 13 decisive role in the formation of O₃ episode before a typhoon landing in southeast China.

14

15 The correlation between O₃ and CO has been widely used to identify sources of tropospheric O₃. When O₃ and CO are positively correlated, O₃ is usually originated from the 16 anthropogenic sources with photochemical reactions (Parrish et al., 1998; Voulgarakis et al., 17 18 2011). A negative correlation of O₃ and CO generally indicates the vertical O₃ transport from the upper atmosphere, where air is poor in CO but rich in O₃ (Moody et al., 1995; Parrish et 19 al., 1998). The correlations between hourly CO and O₃ concentrations measured at 8 sites in 20 XQR are shown over two periods from 12:00 June 11 to 12:00 June 12 and from 12:00 June 21 22 13 to 12:00 June 14, respectively (Fig. 6). In contrast to a significantly positive correlation of 23 the CO and O₃ during the first period, reflecting a dominant role of anthropogenic sources in the O₃ changes (Fig. 6a), the CO and O₃ concentrations were negatively correlated 24 (significantly at P<0.005) during the second period (Fig. 6b), further confirming that the O₃ 25 26 episode with nocturnal high O₃ over XQR was largely contributed by downward transport of 27 O₃-rich air in the peripheral subsidence of Typhoon Hagibis. –For interpreting the higher CO concentrations during the O₃ episode (Fig. 6b) comparing to the CO levels before the O₃ 28 episode (Fig. 6a), we may consider the atmospheric removal of CO by hydroxyl radical (OH). 29 It is well-known that O₃ photolysis produces O¹d, which react with H₂O to produce 2OH, and 30 the reaction of CO with OH quickly forms the stable end product of carbon dioxide (CO₂) 31 (Seinfeld and Spyros, 2006). In the situation of normal photochemical production (Fig. 6a), 32

- 1 high O₃ could lead to more OH production and consequently lower CO. In the situation of
- 2 peripheral O₃-rich air subsidence of the typhoon, the downward dry air (Fig. 4d) with lower
- 3 abundance of OH radicals could decrease the removal of CO. This would result in CO
- 4 accumulation and consequently high CO concentrations, and high CO accumulation within
- 5 boundary layer could overwhelm the dilution of CO-poor air from the UTLS during the high
- 6 O_3 episode.

8

4 Summary

- 9 This observation study presents an O₃ episode due to downward transport from the UTLS to
- 10 surface air in the peripheral TC subsidence over the southeastern coast of China. An
- exceptionally high O₃ event during June 12-14, 2014 was observed with the nocturnal surface
- 12 O₃ levels exceeding 70 ppbv and large enhancements of surface O₃ concentrations by about
- 13 21 ppbv in daytime and up to 42 ppbv in nighttime. The ground observations of O₃, NO₂ and
- 14 CO accompanying meteorology from both observations and reanalysis over XQR during the
- 15 event of Typhoon Hagibis are examined to assess the contributions of chemical production,
- 16 horizontal advection and vertical transport to the O₃ episode.

17

- 18 As the contributions of horizontal advection and chemical production to surface O₃
- 19 enhancement in the O₃ episode are excluded, the peripheral subsiding branches in the TC
- 20 circulation bringing O₃-rich air from the UTLS to surface air are identified to be responsible
- for peaking the surface O_3 levels over the southeastern coast of China during June 12-14,
- 22 2014 before the landfall of Typhoon Hagibis. This rational analysis is further supported by a
 - significantly negative correlation between the surface O₃ and CO as well as the dry surface air
- observed during the O_3 episode.

25

- 26 This case study of Typhoon Hagibis provides observational evidence of TC-driven vertical
- 27 transport of O₃ from the UTLS region to the surface, revealing a significant effect of such a
- 28 process of STE of O₃ on deterioration of air quality. Evidence suggests deep stratospheric
- 29 intrusions can elevate surface O₃ to unhealthy levels before a typhoon landing in southeast
- 30 China. Stratospheric O₃ is a natural source dominating tropospheric O₃ pollution in this

- 1 scenario. Considering the frequency and distribution of TC in the world and their impact on
- 2 STE, this finding has implications on tropospheric O₃ as well as environment and climate
- 3 changes Tropical cyclones, as an important STE mechanism, could exert an enormous impact
- 4 on air mass and energy transports in the troposphere, as well as redistribution of tropospheric
- 5 <u>ozone</u>.

- 7 A pattern of well-organized deep TC convection for the exchange of chemical species
- 8 between the UTLS and surface air is depicted in this case study of TC in southeast China.
- 9 Based on the understanding of the dynamical structure of TC and the chemical distribution in
- 10 the atmosphere, the strong subsiding branches of vertical TC circulation could unusually
- 11 transport the upper O₃-rich air to the surface in any TC events, which is to be further studied
- 12 with more comprehensive observations to characterize the extent to which these UTLS ozone
- 13 enhancements reach the surface. The implications of this finding on environment and climate
- changes need to be explored by using coupled meteorology-chemistry models.

15

16

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- 22 NCEP-FNL meteorological data were freely downloaded from the NOAA-CIRES Climate
- 23 Diagnostics Center, Boulder, Colorado, USA (http://rda.ucar.edu/datasets/).

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References

- 26 Baray, J. L., Ancellet, G., Taupin, F. G., Bessafi, M., Baldy, S., and Keckhut, P.: Subtropical
- 27 tropopause break as a possible stratospheric source of ozone in the tropical troposphere, J.
- 28 Atmos. Sol-Terr. Phy., 60(1), 27-36, doi:10.1016/S1364-6826(97)00116-8, 1998.
- 29 Baray, J. L., Ancellet, G., Randriambel, T., and Baldy, S.: Tropical cyclone Marlene and

- stratosphere-troposphere exchange, J. Geophys. Res., 104(D11), 13953-13970,
- 2 doi:10.1029/1999JD900028, 1999.
- 3 Bellevue, J., Baray, J. L., Baldy, S., Ancellet, G., Diab, R. D., and Ravetta, F.: Simulations of
- 4 stratospheric to tropospheric transport during the tropical cyclone Marlene event, Atmos.
- 5 Environ., 41(31), 6510-6526, doi:10.1016/j.atmosenv.2007.04.040, 2007.
- 6 Betts, A. K., Gatti, L. V., Cordova, A. M., Silva Dias, M. A. F., and Fuentes, J. D.: Transport
- of ozone to the surface by convective downdrafts at night, J. Geophys. Res., 107(D20),
- 8 8046, doi:10.1029/2000JD000158, 2002.
- 9 Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D.,
- Lonneman, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J.,
- 11 Middleton, P., and Wang, T.: Ozone precursors relationships in the ambient atmosphere, J.
- Geophys. Res., 97(D5), 6037-6055, doi:10.1029/91JD03014, 1992.
- Ding, A., Wang, T., Xue, L., Stohl, A., Lei, H., Jin, D., Ren, Y., Wang, X., Wei, X., Qi, Y., Liu,
- J., and Zhang, X.: Transport of north China air pollution by midlatitude cyclones: Case
- study of aircraft measurements in summer 2007, J. Geophys. Res., 114(D8), D08304,
- doi:10.1029/2008JD011023, 2009.
- 17 Donnell, E. A., Fish, D. J., Dicks, E. M., and Thorpe, A. J.: Mechanisms for pollutant
- transport between the boundary layer and the free troposphere, J. Geophys. Res., 106(D8),
- 7847-7856, doi:10.1029/2000JD900730, 2001.
- 20 Duncan, B. N., and Chameides, W. L.: Effects of urban emission control strategies on the
- 21 export of ozone and ozone precursors from the urban atmosphere to the troposphere, J.
- 22 Geophys. Res., 103(D21), 28159-28179, doi:10.1029/98JD02145, 1998.
- 23 Emanuel, K. A.: An air-sea interaction theory for tropical cyclones. Part I: steady-state
- 24 maintenance, J. Atmos. Sci., 43(6), 585-605,
- 25 doi:10.1175/1520-0469(1986)043<0585:AASITF>2.0.CO;2, 1986.
- Fadnavis, S., Berg, G., Buchunde, P., Ghude, S. D., and Krishnamurti, T. N.: Vertical transport
- of ozone and CO during super cyclones in the Bay of Bengal as detected by Tropospheric
- 28 Emission Spectrometer, Environ. Sci. Pollut. Res., 18(2), 301-315,
- 29 doi:10.1007/s11356-010-0374-3, 2011.
- 30 Feng, Y., Wang, A., Wu, D., and Xu, X.: The influence of tropical cyclone Melor on PM₁₀

- 1 concentrations during an aerosol episode over the Pearl River Delta region of China:
- Numerical modeling versus observational analysis, Atmos. Environ., 41(21), 4349-4365,
- 3 doi:10.1016/j.atmosenv.2007.01.055, 2007.
- 4 Grant, D. D., Fuentes, J. D., DeLonge, M. S., Chan, S., Joseph, E., Kucera, P., Ndiaye, S. A.,
- 5 and Gaye, A. T.: Ozone transport by mesoscale convective storms in western Senegal,
- 6 Atmos. Environ. 42(30), 7104-7114, doi:10.1016/j.atmosenv.2008.05.044, 2008.
- 7 Holton, J. R., Haynes, P. H., McIntyre, M. E., Douglass, A. R., Rood, R. B., and Pfister, L.:
- 8 Stratosphere-troposphere exchange, Rev. Geophys., 33(4), 403-439, 1995.
- 9 Hsu, J., and Prather, M. J.: Is the residual vertical velocity a good proxy for
- stratosphere-troposphere exchange of ozone?, Geophys. Res. Lett., 41, 9024–9032,
- doi:10.1002/2014GL061994, 2014.
- 12 Hu, X. M., Fuentes, J. D., and Zhang, F.: Downward transport and modification of
- tropospheric ozone through moist convection, J. Atmos. Chem., 65(1), 13-35,
- 14 doi:10.1007/s10874-010-9179-5, 2010.
- 15 Hu, X. M., Klein, P. M., Xue, M., Shapiro, A., and Nallapareddy, A.: Enhanced vertical
- mixing associated with a nocturnal cold front passage and its impact on near-surface
- temperature and ozone concentration, J. Geophys. Res., 118(7), 2714-2728,
- doi:10.1002/jgrd.50309, 2013.
- 19 Hu, X. M., Klein, P. M., Xue, M., Zhang, F., Doughty, D. C., Forkel, R., Joseph, E., and
- Juentes, J. D.: Impact of the vertical mixing induced by low-level jets on boundary layer
- 21 ozone concentration, Atmos. Environ., 70, 123-130, doi:10.1016/j.atmosenv.2012.12.046,
- 22 2013.
- Huang, J. P., Fung, C. H., Lau, K. H., and Qin, Y.: Numerical simulation and process analysis
- of typhoon-related ozone episodes in Hong Kong, J. Geophys. Res., 110(D5), D05301,
- 25 doi:10.1029/2004JD004914, 2005.
- 26 Huang, J. P., Fung, C. H., and Lau, K. H.: Integrated processes analysis and systematic
- 27 meteorological classification of ozone episodes in Hong Kong, J. Geophys. Res., 111(D20),
- 28 D20309, doi:10.1029/2005JD007012, 2006.
- 29 Jacob, D. J. (1999), Introduction of Atmospheric Chemistry, pp. 234–243, Princeton Univ.
- 30 Press, Princeton, N. J..

- 1 Lelieveld, J. and Crutzen, P. J.: Role of deep cloud convection in the ozone budget of the
- 2 troposphere, Science, 264,793-797, 1994.
- 3 Lin, M., Fiore, A. M., Horowitz, L. W., Langford, A. O., Oltmans, S. J., Tarasick, D., and
- 4 Rieder, H. E.: Climate variability modulates western US ozone air quality in spring via
- deep stratospheric intrusions, Nature, 6, 7105, doi:10.1038/ncomms8105, 2015.
- 6 Liu, J., Tarasick, D. W., Fioletov, V. E., McLinden, C., Zhao, T., Gong, S., Sioris, C., Jin, J. J.,
- 7 Liu, G., and Moeini, O.: A global ozone climatology from ozone soundings via trajectory
- 8 mapping: a stratospheric perspective, Atmos. Chem. Phys., 13, 11441-11464,
- 9 doi:10.5194/acp-13-11441-2013, 2013.
- 10 Moody, J. L., Oltmans, J., and Merrill, T.: Transport climatology of tropospheric ozone:
- Bermuda, 1988–1991, J. Geophys. Res., 100(D4), 7179-7194, doi:10.1029/94JD02830,
- 12 1995.
- Parrish, D. D., Trainer, M., Holloway, J. S., Yee, J. E., Warshawsky, M. S., Fehsenfeld, F. C.,
- Forbes, G. L., and Moody, J. L.: Relationships between ozone and carbon monoxide at
- surface sites in the North Atlantic region, J. Geophys. Res., 103(D11), 13357-13376, 1998.
- 16 Sahu, L. K., and Lal, S.: Changes in surface ozone levels due to convective downdrafts over
- the Bay of Bengal. Geophys. Res. Lett. 33(10), L10807, doi:10.1029/2006GL025994,
- 18 2006.
- 19 Seinfeld, J. H., and Spyros, N. P.: Atmospheric Chemistry and Physics: From Air Pollution to
- 20 Climate Change, 2nd edition, J. Wiley, New York, 2006.
- Tang, Q., Prather, M. J., and Hsu, J.: Stratosphere troposphere exchange ozone flux related
- to deep convection, Geophys. Res. Lett., 38, L03806, doi:10.1029/2010GL046039, 2011.
- Voulgarakis, A., Telford, P. J., Aghedo, A. M., Braesicke, P., Faluvegi, G., Abraham, N. L.,
- Bowman, K. W., Pyle, J. A., and Shindell, D. T.: Global multi-year O₃-CO correlation
- 25 patterns from models and TES satellite observations, Atmos. Chem. Phys., 11, 5819-5838,
- 26 doi:10.5194/acp-11-5819-2011, 2011.
- Weber, R. O., and Prevot, A. S. H.: Climatology of ozone transport from the free troposphere
- into the boundary layer south of the Alps during North Foehn, J. Geophys. Res., 107(D3),
- 29 4030, doi:10.1029/2001JD000987, 2002.

Wu, M., Wu, D., Fan, Q., Wang, B. M., Li, H. W., and Fan, S. J.: Observational studies of the
 meteorological characteristics associated with poor air quality over the Pearl River Delta
 in China, Atmos. Chem. Phys., 13, 10755-10766, doi:10.5194/acp-13-10755-2013, 2013.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S.
M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four
Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem.
Phys., 14, 13175-13188, doi:10.5194/acp-14-13175-2014, 2014.



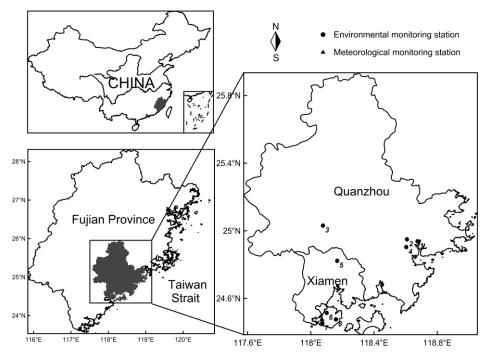


Figure 1. Locations of Fujian Province in China (shaded areas, upper left panel) and the Xiamen and Quanzhou region (XQR) in Fujian Province (shaded areas, lower left panel), and the distribution of 9 monitoring stations (8 environmental sites with black dots numbering from 1 to 8, and 1 meteorological observatory of Xiamen with a black triangle) over XQR (lower right panel).

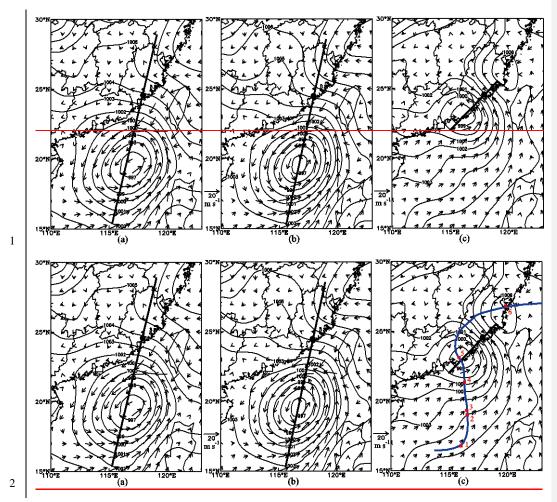


Figure 2. Sea-level air pressure (hPa, contour lines) and 1000 hPa wind vectors of NCEP-FNL data, at (a) 14:00 June 13, (b) 20:00 June 13 and (c) 20:00 June 15, 2014 with black dots representing XQR location. Three straight lines link XQR and the centers of Typhoon Hagibis. The blue curve with the red dots and numbers from 1 to 6 in (c) indicate the typhoon track with the typhoon locations of at 2:00 12 June, 14:00 13 June, 20:00 13 June, 8:00 15 June, 20:00 15 June and 20:00 16 June respectively.

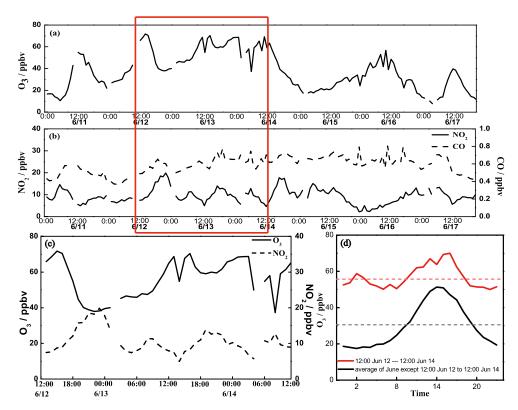


Figure 3. Hourly variations in the 8-site averaged surface concentrations of (a) O₃,(b) NO₂ during June 11-17 with the red rectangular column marking the period of surface O₃ event and (c) O₃ and NO₂ for the surface O₃ event over XQR and (c) O₃ and NO₂ for the surface O₃ event during June 12-14, 2014 over XQR, as well as (d) diurnal changes of surface O₃ from 12:00 Jun 12 to 12:00 Jun 14 (red curve) and in June excluding June 12-14,2014 (black curve) with two dotted lines indicating the daily averaged O₃ concentrations for two diurnal curves.

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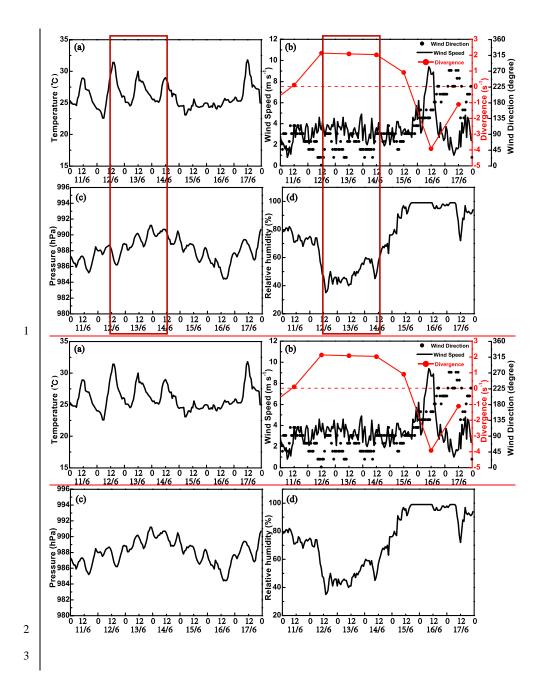
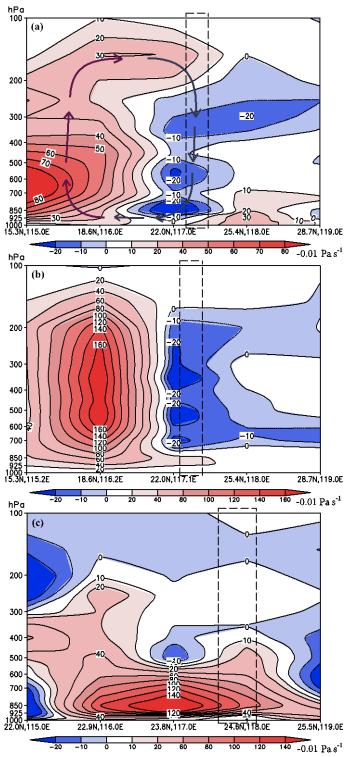


Figure 4. Time series of (a) surface air temperature (b) wind speed, direction and divergence, (c) air pressure and (d) relative humidity observed in the observatory of Xiamen from 11 to 17 June 2014 with the red rectangular columns marking the period of surface O3 event. The red curve in (b) is a daily variation in divergences at 1000 hPa over XQR, calculated with FNL data.

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2 Figure 5. Vertical cross sections of vertical velocity (-0.01Pa $\rm s^{\text{-}1}$) along the three straight

3 lines linking XQR and the centers of Typhoon Hagibis in Figure 2 at (a) 14:00 June 13, (b)

20:00 June 13 and (c) 20:00 June 15, 2014 (FNL data). Two dash boxes denote the location of

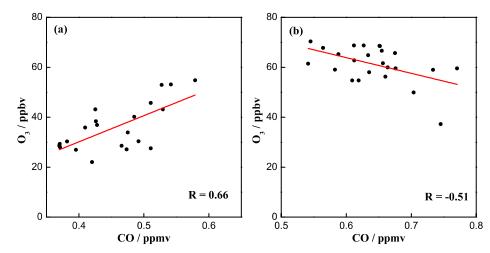
XQR. The lines with arrows indicate the in-up-out-down overturning air flows in the vertical

6 direction of typhoon.



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Figure 6. Correlations between measured surface CO and O_3 over two periods respectively (a) from 12:00 June 11 to 12:00 June 12 and (b) from 12:00 June 13 to 12:00 June 14, 2014, passing the significant level of 0.005. Red lines are the linear fittings.