Atmospheric Environment 47 (2012) 226–235

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Sudden increase in the total ozone density due to secondary ozone peaks and its effect on total ozone trends over Korea

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ARTICLE INFO

Article history:
Received 23 May 2011
Received in revised form
28 October 2011
Accepted 3 November 2011

Keywords:
Total column ozone trend
Secondary ozone peak
Upper troposphere lower stratosphere
Ozone

ABSTRACT

Total column ozone (TCO) amounts observed by the Dobson spectrophotometer from 1985 to 2008 in Seoul and vertical ozone profiles obtained with the ozonesonde from 1995 to 2007 in Pohang were used to investigate the relationship between the occurrence of Secondary Ozone Peak (SOP) in the Upper Troposphere/Lower Stratosphere (UT/LS) layer and the enhancement in TCO over the Korean Peninsula. Based on Hybrid Single-Particle, Lagrangian Integrated Trajectory (HYSPLIT) simulations, the advection of a northern mid-latitudinal ozone-rich airmass from the northwest is closely related to SOP occurrences, which consequently lead to enhancements in the amount of ozone in both the UT/LS and the total column at stations in Korea. In addition, both the frequency of the northwesterly advection and the northern mid-latitudinal ozone amount are revealed to affect the amount of ozone in the UT/LS and total column by up to 7 DU. The relationship between the SOP occurrence frequency and the long-term TCO trend was investigated with observed data collected in all seasons. The UT/LS ozone enhancements, which are largely affected by SOP occurrences, are considered to be positively related to the TCO trend from 1985 to 2008 over the Korean Peninsula.

1. Introduction

Stratospheric ozone plays an important role in absorbing UV radiation from the sun and preserving human health and global biological systems. Furthermore, ozone is an important heating source in the stratosphere (Manabe and Moller, 1961). Since the discovery of the ozone hole in Antarctica (Chubachi, 1984; Farman et al., 1985), the stratospheric ozone trend and its recovery have been one of the most important global issues in the fields of climate and environmental science. For this reason, extensive studies of ozone have been carried out in order to evaluate the global ozone variation with data measured both at ground and satellite-based platforms (e.g., Stolarski et al., 1991; Fioletov et al., 2002). These investigations have also focused on local (e.g., Cho et al., 1994, 2003; Tarasick et al., 1995; Kim et al., 2005) and global ozone trends (e.g., Fishman et al., 1990; Fioletov et al., 2002; Ziemke et al., 2005).

Total column ozone variations are known to be associated with the changes in solar activity (e.g., Angell, 1989; Zerefos et al., 2001; Harris et al., 2003) and natural oscillations (e.g., Angell and Kroshover, 1973; Rood, 1986). After removing these effects, the trend of residuals which were derived from the total column ozone (TCO) was considered to be the ozone layer trend (e.g., Reinsel et al., 1981; Reinsel and Tiao, 1987). However, tropospheric ozone has recently been found to be affected by natural oscillations such as the arctic oscillation (Creilson et al., 2005), and the Stratosphere-Troposphere Exchange (STE) (Kim et al., 2002) in the mid-latitude regions. A previous investigation by Kim et al. (2002) revealed that STE of ozone over Korea is associated with upper trough and surface high pressure system, where downward fluxes of ozone can occur between 100 and 500 h Pa. STE of ozone has a large influence on the vertical ozone profile in the upper troposphere. Hwang et al. (2007) suggested that the subsidence of stratospheric airmass is related to the formation of the Secondary Ozone Peak (SOP) in the Upper Troposphere/Low Stratosphere (UT/LS) over East Asia. Rossby wave breaking induces the intrusion of stratospheric (or tropospheric) ozone, which causes one or several ozone peaks in ozone profiles (Lemoine, 2004).

Hwang et al. (2007) reported that the characteristics of SOP, defined as the maximum in the ozone profile limited to the altitude range of 9–16 km, have the peak with the higher partial pressure in the case of more than one maximum, and found that the frequency

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doi:10.1016/j.atmosenv.2011.11.011

of SOP occurrence increased from 1995 to 2004 based on Halogen Occultation Experiment (HALOE) and ozonesonde observations in Pohang, Korea. Using ozonesonde and SAGE II data since 1969 and 1985, respectively, Lemoine (2004) found that two types of advection resulted in SOP in the UT/LS. The highest SOP occurrence frequency was observed during the period from March through May in Uccle, Europe. It was revealed that the SOP occurrence frequency was highly correlated with the seasonal cycle of TCO in Uccle. Lemoine (2004) used data from February to May to show that STE has a large influence on high-latitudinal TCO changes and also potentially affect long-term ozone trends. However, the effect of SOP formation on TCO trends for East Asia has yet to be investigated.

In the present work, the investigation was conducted, for the first time, to identify the relationship between TCO trends and SOP occurrence in the UT/LS layer at stations in the Korean Peninsula by quantifying enhanced amounts of TCO due to SOP events over a long period. In addition, the mechanisms of SOP formation are examined based on Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) simulations. The effects of the SOP occurrence frequency on the seasonal characteristics of UT/LS ozone and the TCO amount are also investigated.

2. Methods

In this study, the TCO amount and vertical ozone profiles from ozonesonde are used to investigate the relationship between the TCO amount and the SOP occurrence. The TCO data were obtained by the Dobson spectrophotometer from 1985 to 2008 at Yonsei University (37.57° N, 126.95° E, 84 m above sea level, WMO/GO$_3$OS station No. 252) in Seoul, Korea. The Electrochemical Concentration Cell (ECC) ozonesonde was used to measure the vertical ozone distribution from 1995 to 2007 at a station in Pohang (36.02° N, 129.23° E, 6 m above sea level, WMO/GO$_3$OS station No.332), Korea, which is located south of Seoul by about 250 km. The ozonesonde data was obtained from Korean Meteorological Administration (KMA), which has been operating the ozonesonde. The TCO measured since 1985 by the Dobson spectrophotometer was utilized in this study as the TCO data obtained by the Brewer spectrophotometer in Pohang is available only since 1994. In order to validate the relevance of using the TCO data obtained in Seoul and vertical ozone profiles from Pohang, we obtained a ratio of 1.038 ± 0.041 for the monthly averaged TCO obtained with the Dobson in Seoul to that obtained with the Brewer in Pohang (see Fig. 1). The ratio of the monthly averaged TCO with the Dobson instrument to that obtained with the Brewer instrument at Yonsei University was 1.014 ± 0.029. All estimated confidence and denote error bars are determined by 1-sigma uncertainties. The ratio between the TCO in Seoul and that in Pohang, which could be due to the systematic differences between the two instruments, is almost equal to that measured by the two different instruments at collocated site as found in a previous study (Kerr et al., 1988).

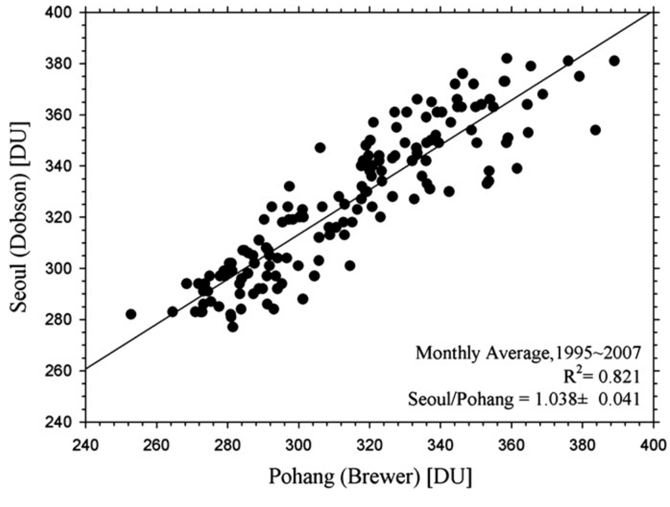

Fig. 1. Comparison of the monthly averaged TCO between the Brewer spectrophotometer in Pohang and the Dobson spectrophotometer in Seoul from 1995 to 2007.

2.1. Data quality of TCO in Seoul

The TCO data obtained with the Dobson spectrophotometer were compared with the data from the Brewer spectrophotometer at the same location and Total Ozone Mapping Spectrometer (TOMS)/Ozone Monitoring Instrument (OMI) from 1999 to 2008 and from 1985 to 2008, respectively (see Fig. 2). The Dobson data exhibits a ratio of 0.989 ± 0.047 (number of data points = 2045) to the values obtained with the Brewer, and a ratio of 1.009 ± 0.050 (number of data points = 6745) to the data from the TOMS/OMI. Such ratios mean the inter-comparison accuracies with respect to the Brewer and the TOMS/OMI are within ±2%. In a previous study, the ratio of the Brewer to Dobson (Brewer/Dobson) was

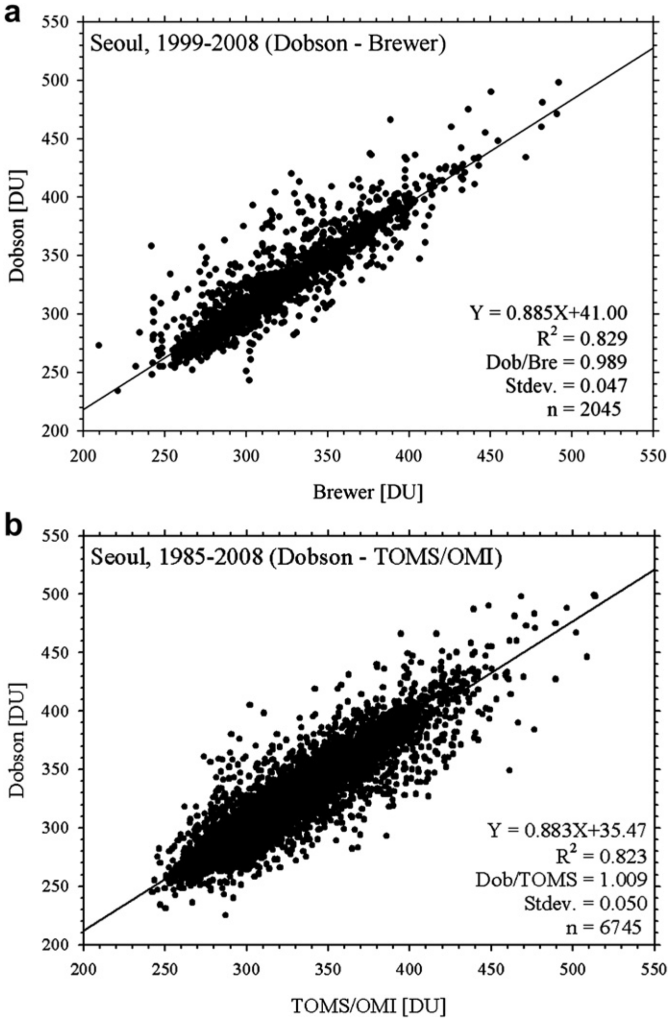

Fig. 2. Comparison of the daily TCO obtained with the Dobson and (a) the Brewer spectrophotometer (Dob/Bre) from 1999 to 2008 (number of data points: 2045), and (b) the TOMS/OMI from 1985 to 2008 (number of data points: 6745) in Seoul.

0.989 ± 0.029 over a period from 2005 to 2006 for direct sun measurements, and 0.983 ± 0.097 for the period from 1999 to 2006 (Kim et al., 2007). The slope of the Dobson to the TOMS/OMI data for the TCO was 0.92, with an intercept of 24.80 DU ($R^2 = 0.91$), for the period from 1985 to 2004 (Kim et al., 2005).

2.2. Determination of SOP occurrence in Pohang

Ozonesonde is a balloon-borne observing instrument used to measure the vertical distribution of ozone mixing ratio and meteorological parameters (e.g., temperature and pressure), simultaneously. In Korea, vertical profiles of ozone have been observed by ozonesonde only at the Pohang station of the KMA on a weekly basis since April 1995. 5A ECC type soundings have been used at the site. In a previous study, the inaccuracy of ECC type soundings in the troposphere was less than 4% when compared with data from a UV absorption photometer (Reid et al., 1996). In addition, Kivi et al. (2007) also reported that the ECC type sounding data are dependent on the altitude within inaccuracies of 5%.

To determine the height and amplitude of the SOP, the measured data were interpolated with 0.1 km intervals. In the present study, the SOP is defined as a layer of ozone-rich air with a finite height where the ozone partial pressure is at least 10% of that at the primary peak; this layer is separated from stratospheric ozone by a layer of ozone-poor air. Since these regressions were carried out after smoothing the ozone vertical distributions observed at the Pohang site, the peaks with smaller-scale perturbations and random observation errors were eliminated using the regressed ozone vertical distribution data. The height of the SOP is restricted to a range of 9–16 km, the UT/LS layer, as in a study by Hwang et al. (2007). The altitude interval of UT/LS layer in this study covers the annual variation of tropopause height, which has been known to vary from 9 to 15 km in Korea in winter and summer, respectively (Hwang et al., 2007). In non-SOP cases, the ozone mixing ratio is relatively homogeneous at UT/LS layer. Therefore, seasonal variations in the UT and LS apportionment in the altitude interval from 9 to 16 km does not affect UT/LS ozone amount significantly. Additionally, this altitude interval also covers the ozone change due to the SOP at UT/LS layer. From 1995 to 2007, the SOPs were found in 343 cases out of a total of 594 soundings, which accounts for 57.7%. In previous study by Hwang et al. (2007) with the same definition of the SOP, the SOP occurrence was 44.4% in Pohang from 1995 to 2004.

2.3. Effect of natural oscillation for trend analysis

For the study of the TCO trend, the effect of natural oscillations from the time series was taken into account (cf. Bojkov et al., 1990; Logan et al., 1999; Fioletov et al., 2002). The most dominant cycle of ozone change is seasonal due to the strength change of the Brewer-Dobson circulation. Thus, deseasonalized data are obtained by subtracting the monthly average of TCO from that in a given month.

Regarding the natural oscillation, Solar Cycle (SC) and Quasi-Biennial Oscillation (QBO) influence the stratospheric ozone amounts thus the trend (Bojkov et al., 1990; Logan et al., 1999). Bojkov et al. (1990) incorporated SC and QBO in the model to estimate the long-term TCO trend. Logan et al. (1999) used SC and QBO for the statistical trend models of stratospheric ozone near 90 h Pa. Furthermore, these natural factors affect the long-term ozone trend (e.g., Fioletov et al., 2002; Newchurch et al., 2003a). These two natural oscillations have been well known to explain the substantial part of total ozone variability (e.g., Bowman, 1989; Hamilton, 1989; Chandra and Stolarski, 1991; Zerefos et al., 1992; Yang and Tung, 1994; Randel and Cobb, 1994; Chandra and McPeters, 1994; Bojkov and Fioletov, 1996; Logan et al., 1999; WMO, 1999). This study considered QBO and SC as major natural effects for analyzing the TCO trend. The monthly based data of solar radio flux F10.7 were used to describe the SC, and the monthly based data of zonal wind in 30 h Pa at tropical region were used as the indices for QBO.

3. Results

3.1. Sudden increase in the ozone

A sudden increase in the TCO by more than 40–50 DU in one to two days has occasionally been observed in Seoul from late winter to early spring. The enhancement value is more than 10% of the mean TCO. Comparable enhancements have also been noted in previous studies (Miyagawa and Akagi, 2007). As observed in the work by Miyagawa and Akagi (2007), this TCO enhancement is maintained for a few hours or days.

The TCO enhancement is thought to be associated with local and regional SOP events. The dynamic transport of ozone to the measurement location, the Korean Peninsula, was characterized by the previous study (Kim et al., 2002), which reported that SOP events are the phenomenon of STE of ozone due to the strong zonal wind speed of jet stream around the Korean Peninsula. A time series of the TCO in Seoul and selected examples of ozone vertical distributions observed in Pohang are shown in Fig. 3. The TCO enhancement event was observed at both Seoul and Pohang sites by Dobson and Brewer, respectively, during the period as shown in Fig. 3. Shown in Fig. 3(a) is the time series of TCO in Seoul and Pohang from March through April 2006, where large changes in TCO were frequently observed. SOPs with a large magnitude were simultaneously detected in the UT/LS layer by ozonesonde in Pohang on March 22nd, 29th, and April 28th (see Fig. 3(b)–(d)). The TCO increased suddenly by 37 DU on March 22nd, 55 DU on March 29th, and 20 DU on April 28th when compared to the ozone amount on March 21st, 27th, and April 27th, respectively. In Fig. 3(e), total number of enhancements larger than 20 DU was observed to be 138 cases out of 281 SOP cases and 43 cases out of 212 non-SOP cases for the period from 1995 to 2007. The threshold of 20 DU was obtained from the 1-sigma standard deviation of TCO variation obtained from Dobson data in Seoul. The enhancement in the SOP cases is significantly higher than that in the non-SOP cases. Therefore, these SOP events in the UT/LS, which are related to synoptic weather conditions over East Asia, are thought to contribute to an increase in TCO amounts.

In order to investigate the SOP occurrence mechanism, trajectory calculations were first carried out on the dates of the SOP episodes. Fig. 4 shows 72-h backward and forward trajectories from Seoul during the period from March 26th to 29th, as calculated with the NOAA HYSPLIT model using NCEP reanalysis data. Back and forward trajectory simulations at the altitudes of 20 km using the HYSPLIT model were conducted to compare characteristics of airmass movements at 10 and 15 km where UT/LS layers are present with those at 20 km above the UT/LS layers. As shown in Fig. 3, the TCO amounts significantly increased to 426 and 407 DU on March 28th and 29th, respectively, when compared to the TCO amounts of 363 and 352 DU observed on March 26th and 27th, respectively. An SOP, with a maximum partial pressure of 15.7 mPa was observed with an ozonesonde in Pohang on March 29th, which is considered to be related to the increased TCO amount in Seoul.

Fig. 4 shows changes in the dominant airmass flow patterns from west-east to north-south in the layer between 10 and 20 km

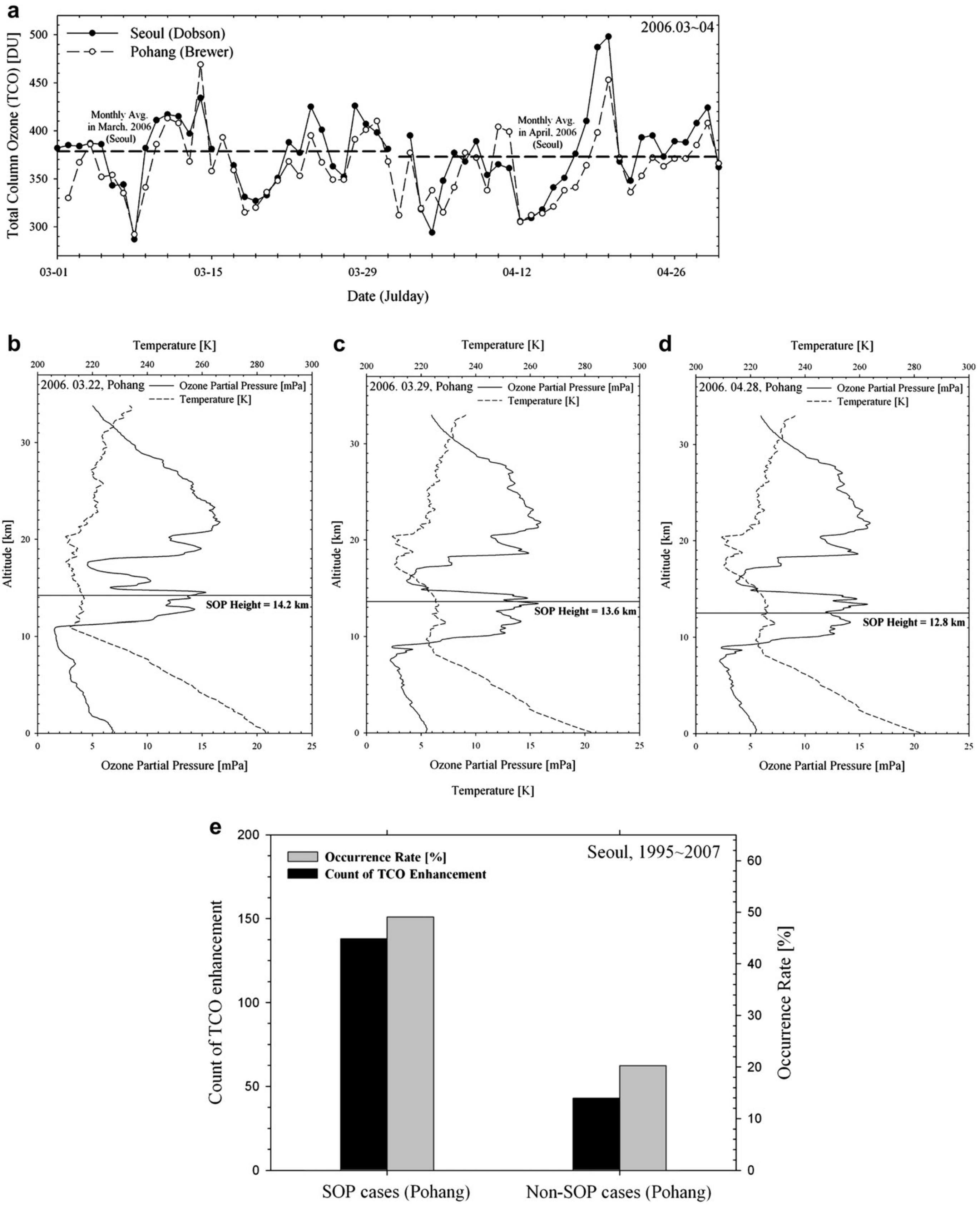

Fig. 3. (a) Time series of the TCO from March to April 2006 in Seoul by Dobson, and in Pohang by Brewer, (b) vertical profiles of ozone partial pressure (solid line) and temperature (dashed line) on March 22nd, (c) March 29th, and (d) April 28th 2006 in Pohang, and (e) count and rate of TCO enhancement occurrence for the SOP and the non-SOP cases.

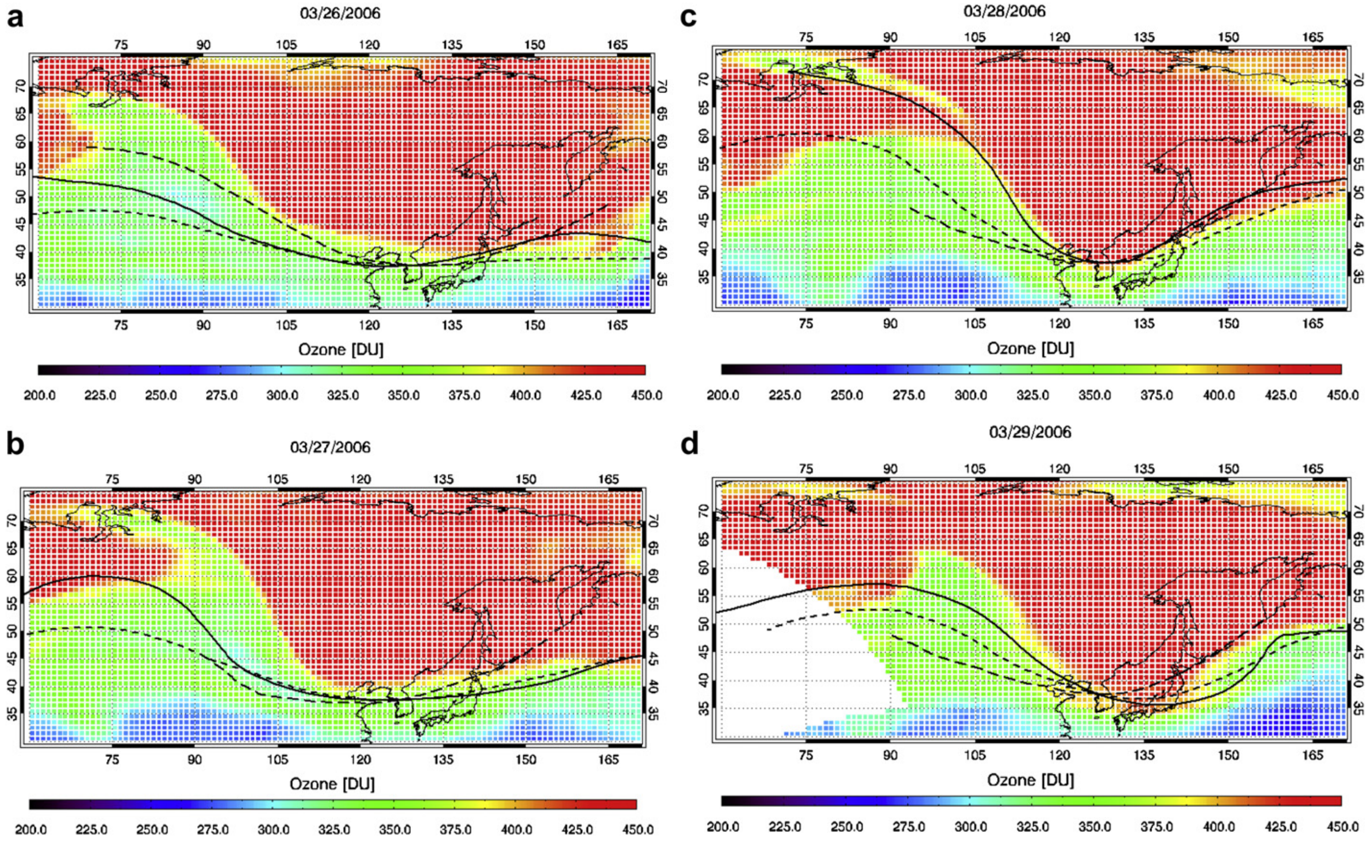

Fig. 4. 72-h back and forward trajectories of an airmass passing through Seoul on (a) 26th, (b) 27th, (c) 28th, and (d) 29th of March 2006 (Solid line: 10 km, Dashed line: 15 km, Long-dashed line: 20 km altitudes).

when ozone enhancement was observed in Fig. 3(a). At the same time, the high value of TCO plume, obtained from Level 3 data of OMI, was also observed over East Asia. The "meridional" flow pattern is related to the inflow of airmass from northern mid-latitude to the UT/LS layer in East Asia. The monthly frequencies of the airmass flow direction in Seoul from 1985 to 2008 and the SOP occurrences in Pohang from 1995 to 2007 are shown in Fig. 5. From January to June, northwesterly (NW) airmass flow patterns were simulated to be dominant over Seoul. The monthly variations in occurrence frequency of NW airmass patterns are similar to those of SOP occurrence frequency. The highest SOP occurrence frequencies ranging from 92.5% to 95.8% were observed from January to April, while the SOP occurrence frequencies ranging from 7.0% to 17.3% were observed from July to September. The monthly frequency of the NW airmass flow pattern at the altitude of 10 km is found to be correlated with SOP occurrences from 1995 to 2007 with a correlation coefficient (R) of 0.92. For this reason, both the highest ozone amount in the northern mid-latitudinal region and the frequency of NW airmass flow patterns are considered to be the causes of the highest SOP occurrence frequency from January to April in Pohang, while both the lowest ozone amount in the northern mid-latitudinal region and the lowest frequency of NW airmass patterns are considered to be the causes of the lowest SOP occurrence frequency observed between July and September in Pohang. However, the SOP occurrence frequency decreased in May and June when compared to that observed from January to April due to both relatively lower polar ozone amounts (Bowman and Krueger, 1985; Bojkov, 1988; Bojkov et al., 1994) and the lower NW flow frequencies.

Shown in Fig. 6 is a comparison of statistical distributions of latitude for the airmass of backward and forward trajectories over Seoul for the enhanced to normal cases, as calculated with the HYSPLIT model. In the figure, the TCO was classified into high (H-TOZ) and normal TCO (N-TOZ) cases. The latitudinal distributions were quantified at altitudes of 10, 15, and 20 km. Start and arrival locations for the 72-h backward and forward trajectories, respectively, in the H-TOZ cases were found to be located at higher latitudes than those for the N-TOZ cases. Furthermore, the differences in the mean latitudes of the starting locations were found to become larger as the trajectory run time increase, which means the origin of the airmass is the northern mid-latitudinal region for the H-TOZ cases. Similarly, the airmass passes through the Korean Peninsula to the northern mid-latitudinal region. However, for the case of altitude of 20 km, these tendencies have been weak compared with the cases of altitudes of 10 and 15 km. In a t-test analysis, these differences in the latitudinal distributions are shown to be statistically significant with a p-value less than 0.01.

The seasonal variation of SOP over Korea is similar to the UT/LS variation of ozone over North America as described by Newchurch et al. (2003b). A linear correlation between TCO anomalies and the UT/LS ozone amount in SOP and non-SOP cases is shown in Fig. 7. An anomaly in the TCO denotes a daily change in the TCO obtained by subtracting the monthly average TCO from the daily value. Correlation coefficients (R) in the SOP and non-SOP cases were estimated to be 0.53 and 0.29, respectively. As discussed by Hwang et al. (2007), SOP at UT/LS layer is formed below the main ozone peak in the stratosphere so that TCO amount can be enhanced by addition of ozone amount due to SOP in this region. Thus, the larger

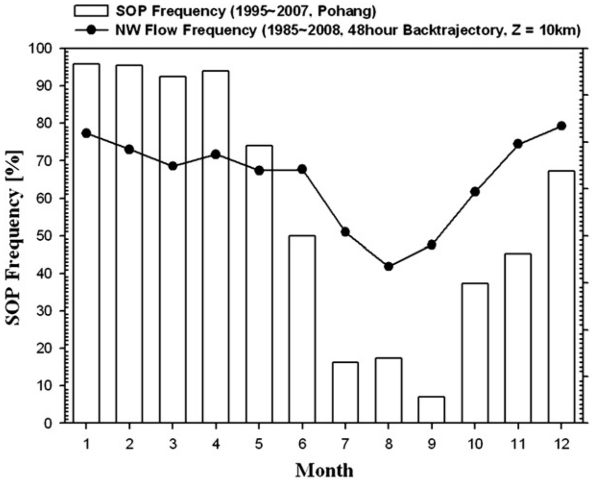

Fig. 5. Monthly frequencies of the airmass flow direction in Seoul from 1985 to 2008, and that of SOP occurrence in Pohang from 1995 to 2007.

correlation coefficients (R) obtained from comparison between UT/LS ozone amount and TCO amount in SOP cases than that in non-SOP case can be attributed to the addition of ozone amount due to SOP in this region. For this reason, SOP events are considered to contribute to an enhancement in the TCO in both the UT/LS and the total column, simultaneously.

3.2. Effects of SOP occurrence on TCO

3.2.1. Seasonal variation of SOP effects

As discussed in the previous section, SOP formation results in an increase in the TCO amount due to a column ozone enhancement in the UT/LS. Over North America, the averaged total ozone for May 1998 is over 45 DU higher than the average total ozone for May 1997–2002 due to the high number of STE events due to SOP occurred (Newchurch et al., 2003b). In order to quantify the influence of the SOP on the TCO amount, we calculated the difference between column ozone amounts in the UT/LS for SOP and non-SOP cases using the ozonesonde data for the period from 1995 to 2007. This difference can be assumed to be an increase in the TCO amount due to the SOP. The average difference in the UT/LS column ozone amount was calculated to be 24.1 DU, which was used as a threshold value to identify the TCO enhancement due to the UT/LS column ozone enhancement. This threshold was used to compare the daily TCO change so that seasonal variations in the UT/LS ozone can be negligible. However, in order to use the difference value as such a criterion, the magnitude of temporal variations in the stratospheric ozone amount must be smaller than 24.1 DU. The perturbation of stratospheric ozone, which is defined as the TCO amount integrated in the 19–29 km layer, was obtained from standard deviations of the stratospheric ozone when assuming a normal distribution. The skewness and kurtosis of stratospheric ozone at the layer from 19 to 29 km, were estimated to be −0.751 and 5.507, respectively (number of data = 524, period of from 1995

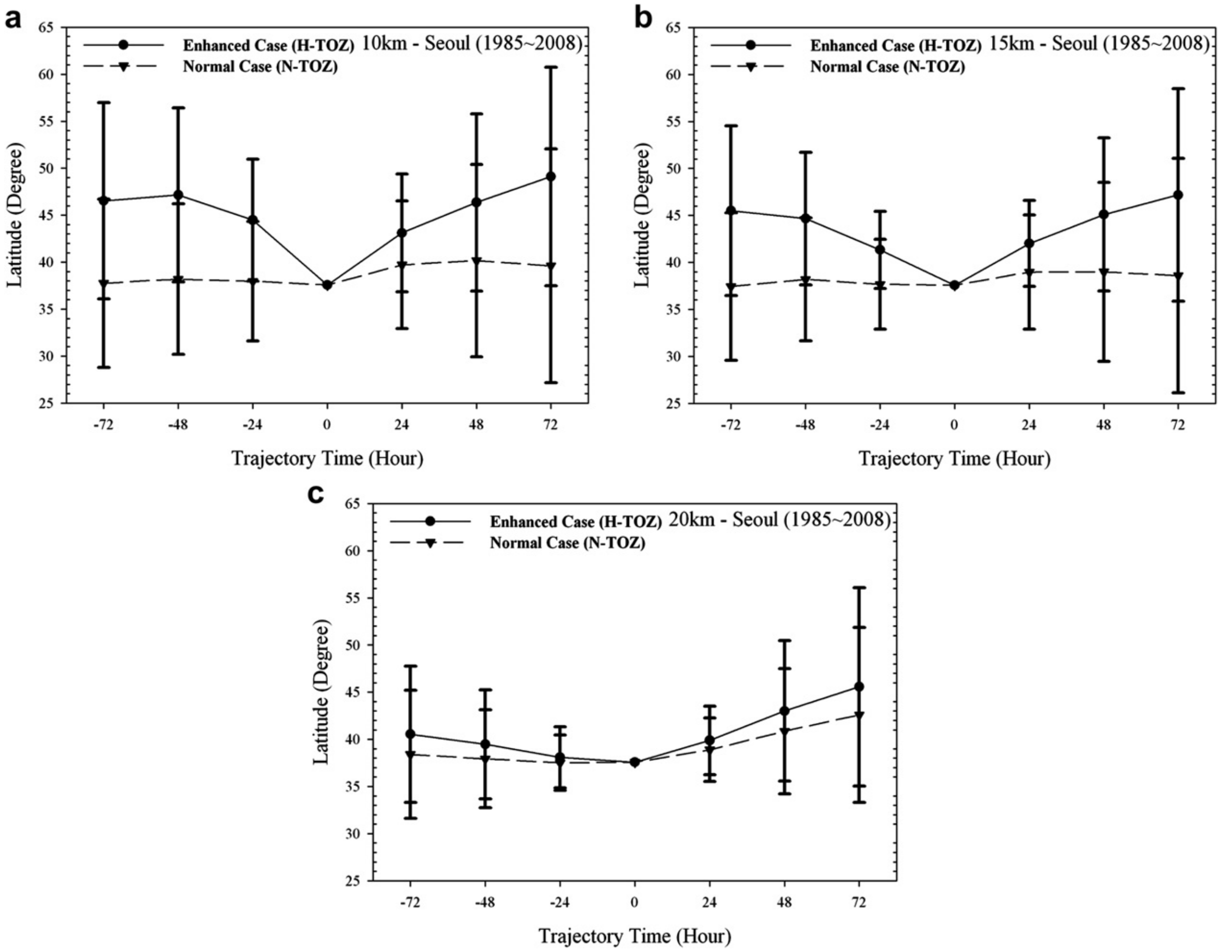

Fig. 6. Mean and deviation of the trajectory latitude results separated by normal TCO (normal case, dashed line) and high TCO (enhanced case, solid line) cases in Seoul, from 1985 to 2008 at altitudes of (a) 10 km, (b) 15 km and (c) 20 km (Error bar is standard deviation of 1-sigma).

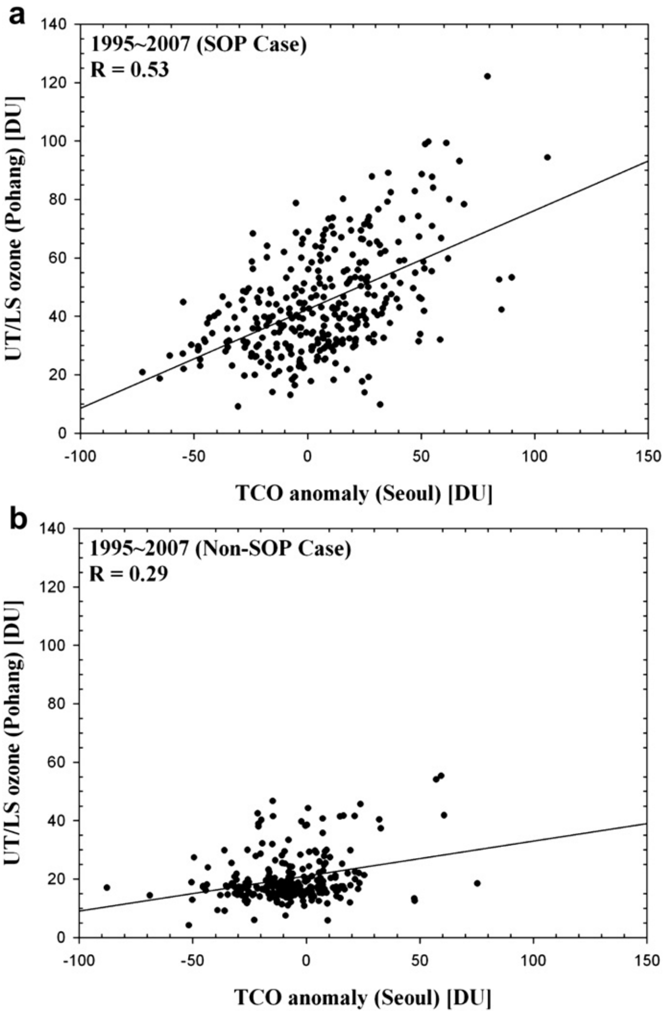

Fig. 7. Correlation between the TCO anomaly with respect to the monthly mean and the UT/LS ozone in (a) SOP and (b) non-SOP cases.

to 2007). We carried out the Jarque–Bera test, which has been used to verify the normal distribution of a dataset. The stratospheric ozone could be assumed to have the normal distribution as *p*-value obtained from the test was smaller than 0.0001. The bottom altitude of 19 km was used instead of 16 km to estimate stratospheric column ozone amount in order to avoid SOP contributions to perturbation of stratospheric ozone though there can be a degree of underestimation in estimated stratospheric column ozone amount by excluding ozone amount between 16 and 19 km altitudes. We also calculated the statistical probability for a perturbation larger than the threshold value of 24.1 DU. The perturbation of stratospheric ozone was calculated to be 13.4 DU. The probability for a perturbation larger than the threshold value was found to be only 3.6%. Even during the period from January to April, when the occurrence frequency of the SOP is highest, the perturbation value was calculated to be 11.6 DU. The probability for a perturbation larger than the threshold was found to be only 2% during the season with the highest SOP occurrence frequencies. Therefore, the short-term TCO change is dominated by the UT/LS ozone change and thus, the perturbation of stratospheric ozone can be ignored.

TCO values were categorized into enhanced UT/LS ozone (ETO) and ordinary UT/LS ozone (OTO). In this study, the ETO case is defined as a day when the TCO change, as compared with the TCO amount of the past non-episodic day closest to the date of interest, is larger than 24.1 DU. The differences between the monthly TCO values averaged when including (I-ETO) and excluding ETO (E-ETO) periods are shown in Fig. 8. From winter to spring, the difference was found to be over 4 DU, with the largest difference of 7.1 DU being observed in March. On the other hand, the difference in autumn was smaller than 2 DU and the smallest value of 0.8 DU was observed in September. These temporal characteristics of the difference values largely depend on the seasonal cycle of the SOP occurrence frequency ($R = 0.96$). The seasonal variations in the SOP have significant effects on the monthly as well as long-term TCO trends. Thus, these trends are influenced by the UT/LS ozone trend to a certain degree.

Lemoine (2004) analyzed the effect of UT/LS ozone on the TCO trend in the spring from February to May. However, in the present study, only 50.7% of the SOPs were observed in the spring, which covers the period from February to May at the station in Korea, while 49.3% of the SOPs were detected in other months. In the months from January through May, 64.1% of the SOPs were observed. The monthly averaged UT/LS ozone enhancement due to the SOP occurrence was quantified using the following expression

$$\Delta[\mathrm{O_3}]_i = P_i\left([\mathrm{UT/LS\ O_3}]_{i,\mathrm{SOP}} - [\mathrm{UT/LS\ O_3}]_{i,\mathrm{non-episode}}\right) \quad (i = \mathrm{months}, 1 \sim 12) \tag{1}$$

where P_i denotes the ratio of the SOP occurrence frequency to the total number of ozonesonde observations in the *i*-th month, and $[\mathrm{UT/LS\ O3}]_{i,\mathrm{SOP}}$ and $[\mathrm{UT/LS\ O3}]_{i,\mathrm{non\text{-}episode}}$ denote the monthly averaged UT/LS ozone column densities measured during SOP events and non-episodic periods, respectively, in the *i*-th month. Based on (1), average $\Delta[\mathrm{O_3}]$ for January–May and other months was calculated to be 14.8 DU and 4.3 DU, respectively. A noticeable UT/LS ozone enhancement due to SOP occurrence in months other than spring was found to account for 27.8% of that calculated for the spring period. Therefore, given high SOP occurrence frequencies as well as a noticeable UT/LS ozone enhancement due to SOP occurrence in months other than spring, the SOP effect on the TCO trend must be investigated over all seasons.

3.2.2. Relationship between TCO trends and SOP occurrence

In order to quantify the difference between the TCO trend with and without enhancement, the monthly averaged dataset and long-term trends for the TCO were reconstructed using TCO data corresponding to the OTO case. Two methods (M1 and M2) were employed to estimate the long-term ozone trend. The M1 method is considered only the seasonal variation of TCO. The trend was estimated by the residuals, which were obtained from subtracting the long-term seasonal variation from TCO. In addition to deseasonalization, linear regressions of the M2 method were also carried out between a dataset of deseasonalized TCO and natural oscillation datasets so as to eliminate QBO and SC effects from the deseasonalized TCO. QBO data with a ten-month lag were employed for the regression since the QBO is known to have an optimal time lag (WMO, 1999; Kim et al., 2005). These methods are summarized in Table 1. The trends are estimated by the residuals, which denotes the difference between the observed TCO and those estimated using regression models. The time series difference that denotes the difference between residual in past and that in present, was used to consider the serial dependence of residuals. The long-term trends of the time series differences were calculated to be smaller than 0.01% for the both M1 and M2. Therefore, the serial dependences were turned out to be negligible for the trend studies about M1 and M2.

The occurrence counts of TCO enhancement with their trend from 1985 to 2008 in Seoul are shown in Fig. 9. During the entire observation period, the counts of enhancement exhibit an

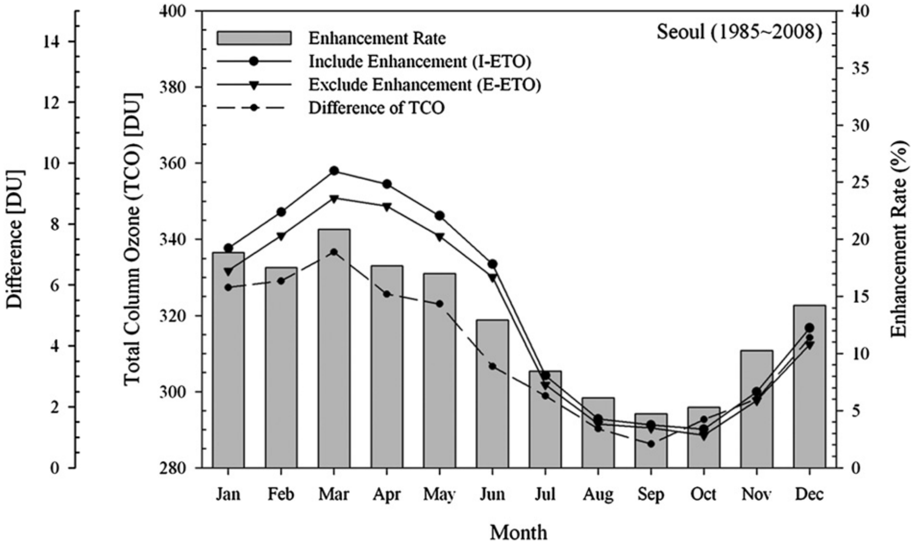

Fig. 8. Difference in the monthly averaged TCO between I-ETO and E-ETO cases in Seoul (1985–2008).

increasing trend annually with correlation coefficient of 0.52. An increasing trend in the enhancement occurrence can influence the long-term TCO trend in a positive manner because the enhancement is expected to contribute to an increase the TCO amount.

Long-term TCO trends can be estimated with M1 and M2, respectively. The long-term TCO trends for the cases of I-ETO and E-ETO for different methods are shown in Fig. 10. A large TCO residual of 386 DU was observed early in 1986. According to a previous report from JMA (2010), the high value of TCO residual was also observed in Tsukuba and Sapporo early in 1986. Larmarque and Hess (2004) reported that arctic oscillation is negatively correlated with the tropospheric ozone amount in springtime over northern hemisphere. Thus, this high TCO values measured over East Asia in early 1986 might be influenced by the lowest arctic oscillation value during the period from 1985 to 2008. The TCO trends as estimated by M1, for cases with ETO (I-ETO) and without ETO (E-ETO) were 1.23 and 0.93% per decade, respectively. The trends as estimated by M2, in the I-ETO and E-ETO cases were 1.17 and 0.89% per decade, respectively. Differences between the TCO trends for the I-ETO and E-ETO cases were found to be 0.30% per decade by M1 and 0.28% per decade by M2. The two sampled *t*-test (Student's *t*-test) shows that the trend difference between I-ETO and E-ETO is highly significant, as estimated by M1 and M2, respectively ($P < 0.001$, two-tailed test). This implies that the increasing trends in UT/LS ozone due to SOP contribute to an increasing trend in the TCO by about 25%.

Table 1
Summary of selected variables and long-term TCO trend for each method.

Method	Selected variables	Trend [%/decade] (1-sigma error)		Trend Difference [%/decade]	Confidence Level
		I-ETO	E-ETO		
Method 1 (M1)	Monthly Mean	1.23 (0.30)	0.93 (0.30)	0.30	$P < 0.001$
Method 2 (M2)	Monthly Mean QBO (10month lag) Solar Cycle (No lag)	1.17 (0.29)	0.89 (0.29)	0.28	$P < 0.001$

*Number of Data = 288 (24 years, 1985–2008).

4. Conclusions

The formation mechanism of the SOP and its effect on TCO trends were examined using the data of the long time series from a Dobson spectrophotometer and an ozonesonde over the Korean Peninsula during the periods from 1985 to 2008 and from 1995 to 2007, respectively. Both a high ozone amount in the northern mid-latitudinal region and the frequency of NW airmass advection are considered to be the causes of the enhancements in the ozone amount both in the UT/LS due to SOP and the total column during winter and spring in the mid-latitudes. In addition, the correlation coefficient in the SOP cases is 0.53 when using the anomaly of the TCO data, which is explicitly larger than those of the non-SOP cases by 0.29. Thus, a rapid enhancement in the TCO can be partially attributed to UT/LS ozone enhancement through SOP events.

Seasonal variations in SOP events were found to have significant effects on the monthly and long-term TCO trends. The average change in the TCO amount due to SOP events during the period from January to May was observed to be larger than 4 DU, with the largest value observed to be 7.1 DU in March. However, the average

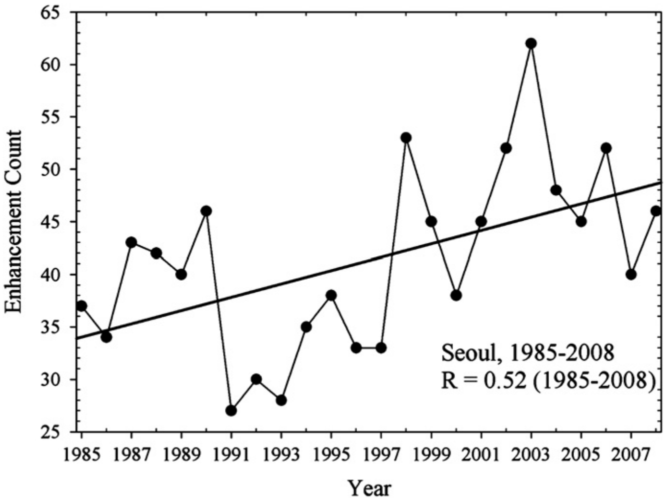

Fig. 9. Long-term trend in the TCO enhancement count from 1985 to 2008 in Seoul.

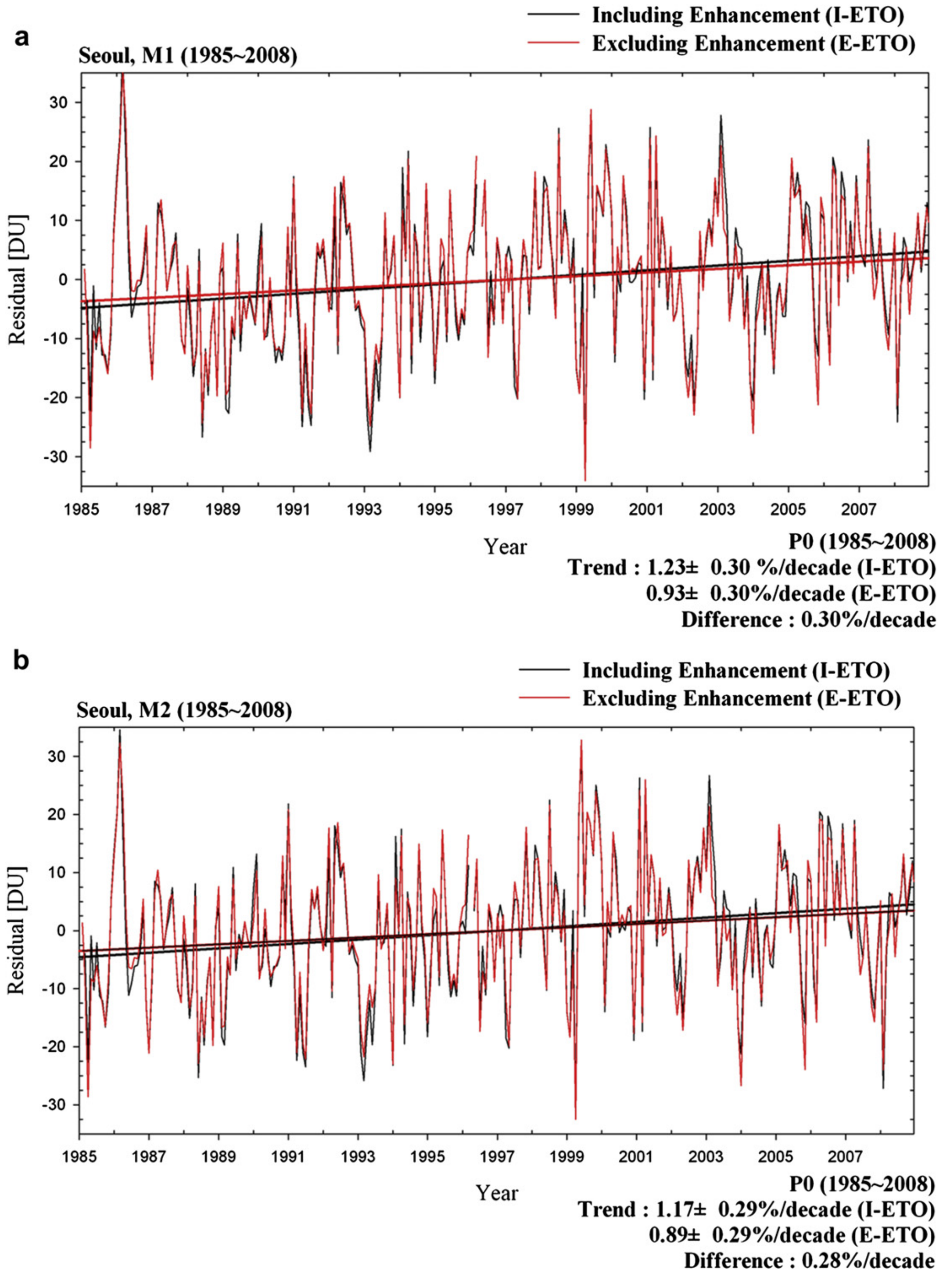

Fig. 10. Long-term TCO trend estimated by (a) M1 and (b) M2 in Seoul (trend uncertainty is standard deviation of 1-sigma).

change in the TCO amount due to SOP events during the period from August to October was observed to be smaller than 2 DU.

The TCO trends were compared for the cases of I-ETO and E-ETO during different time periods between 1985 and 2008. Differences between the TCO trends for M1 in the I-ETO and E-ETO and those for M2 were 0.30 and 0.28% per decade, respectively. The TCO increases as a result of ozone enhancement in the UT/LS mainly due to the increased frequency of SOP occurrence. The difference clearly reflects the trend in ozone enhancement frequencies. It can be concluded that a temporal change in the sudden increase of TCO due to UT/LS ozone enhancement is believed to be a cause of an increasing TCO trend at stations in Korea.

Acknowledgments

This research was supported by the Korean Meteorological Administration Research and Development Program under Grant CATER 2006-3203. This research was partially supported by the

Brain Korea 21 (BK21) program. We thank the Korean Meteorological Administration (KMA) for the ozonesonde datasets at Pohang site and the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT model used in this research.

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