ABSTRACT

In the Mexico City Metropolitan Area (MCMA), ozone ($O_3$) concentration is still higher than in other urban areas in developed countries. In order to reveal the current state of photochemical air pollution and to provide data for validation of chemical transport models, vertical profiles of meteorological parameters and ozone concentrations were measured by ozonesonde in two field campaigns: the first one, during the change of season from wet to dry-cold (November 2011) and the second during the dry-warm season (March 2012). Unlike previous similar field campaigns, ozonesonde was launched twice daily. The observation data were used to analyze the production and distribution of ozone in the convective boundary layer. The observation days covered a wide range of meteorological conditions, and various profiles were obtained. The evolution of the mixing layer (ML) height was analyzed, revealing that ML evolution was faster during daytime in March 2012 than in November 2011. On a day in November 2011, the early-morning strong wind and the resulting vertical mixing was observed to have brought the high-ozone-concentration air-mass to the ground and caused relatively high surface ozone concentration in the morning. The amount of produced ozone in the MCMA was estimated by taking the difference between the two profiles on each day. In addition to the well-known positive correlation between daily maximum temperature and ozone production, effect of the ML height and wind stagnation was identified for a day in March 2012 when the maximum ground-level ozone concentration was observed during the two field campaigns. The relatively low ventilation coefficient in the morning and the relatively high value in the afternoon on this day implied efficient accumulation of the $O_3$ precursors and rapid production of $O_3$ in the ML.

Key words: Field campaign, Ozone, Ozonesonde, Mexico City Metropolitan Area, Mixing layer

1. INTRODUCTION

Recently, the Latin American region has experienced a rapid and uncontrolled economical growth especially in its urban centers, resulting in poor atmospheric environments. The Pan American Health Organization reports that more than 100 million people in the Latin American cities are exposed to levels of air pollution that exceed the recommended standards (World Bank, 2006). As a typical example, Mexico City was called the most polluted place on the planet around 1990 (Mage et al., 1996). However, implementation of mitigation measures such as introduction of low-sulfur fuel, factory relocation and emission regulation have led to substantial decrease in the concentrations of criteria pollutants such as nitrogen dioxide ($NO_2$), carbon monoxide ($CO$), and sulfur dioxide ($SO_2$).

Concentrations of ozone ($O_3$) and PM$_{10}$ (particulate matter with aerodynamic diameter less than 10 micrometers) generated by secondary production, remain high and often exceed the Mexican environmental standard (0.08 ppm 8-h average for $O_3$ and 120 μg m$^{-3}$ daily average for PM$_{10}$). The numbers of days per year exceeding the environmental standards are still more than 100 for $O_3$ and more than 40 for PM$_{10}$ even though the numbers decreased considerably from above 200
for O₃ and 100 for PM₁₀ before the year 2000.

It can be said that the air-pollution level in Mexico City is between that in early-stage developing countries where primary pollutants are of major concern and that in developed countries where secondary pollutants are more important. Considerable efforts have been paid to understand the generation of secondary pollutants, but our understanding has not yet reached a level where scientific knowledge can be efficiently applied to mitigation measures.

In this study, we focus on O₃. Among various trace constituents in the lower atmosphere, O₃ is considered one of the most important substances because it acts as a major oxidizing agent involved in the formation of particulate matter, is a green-house gas, affects the growth of plants, and has by itself deteriorating effects on human health.

In the Mexico City Metropolitan Area (MCMA), many field campaigns on air quality have been carried out in the past. Representative ones are MARI (Mexico City Air Quality Research Initiative; Streit and Guzman, 1996); IMADA-VER (Investigación sobre Materia Partículada y Deterioro Atmosférico - Aerosol and Visibility Evaluation Research; Doran et al., 1998); MCMA-2002 and 2003 (Mexico City Metropolitan Area field campaign; Velasco et al., 2008; Molina et al., 2007; de Foy et al., 2006); MILAGRO-2006 (Megacity Initiative: Local And Global Research Observations; Voss et al., 2010; Rivera et al., 2009; Zhang and Dubey, 2009). In these campaigns, vertical profiles of O₃ concentration and meteorological parameters such as temperature (T), relative humidity (RH), wind speed (WS), and wind direction (WD) were measured by radiosondes, ozonesondes, tethered balloons, or wind profilers. Table 1 lists representative reports on vertical profile measurements.

In February 2002 and April 2003, Velasco et al. (2008) investigated the vertical distribution of O₃ and the influence of the evolving mixing layer (ML) in the MCMA by a tethered balloon system (as part of the

| Field campaign | Methods | Approximate maximum altitude | Measured quantities | Period of study and sampling frequency | Focus |
|---------------|---------|------------------------------|--------------------|--------------------------------------|-------|
| MARI          | Radiosonde, tethered balloon, ozonesonde, and LIDAR | 3 km AGL (LIDAR), 1 km AGL (other methods) | WD, WS, T, RH, and O₃ | September 1990, February 1991, March 1992, and March 1993. Radiosondes at 06:00 and 18:00 LST. Tethered balloon every 3 h. | Vertical distribution of O₃ and the relationship to drainage and gap flows from outside of the Mexico City basin. |
| IMADA-VER     | Radiosonde, radar wind profiler, and sodar | 3 km AGL (radar wind profiler), 100 m AGL (sodar) | WD, WS, T, and RH | From 23 February to 22 March 1997 excluding Sundays (08:00, 11:00, 13:30, 16:30, and 19:30 LST) | Transport and diffusion behaviors of airborne pollutants, and their relationship to the vertical profiles of wind and temperature |
| MCMA-2002 & 2003 | Tethered balloon, pilot balloon, radiosonde, and sodar | 1 km AGL (tethered balloon), 0.6 km AGL (sodar) | O₃, T, RH, WS, and VOCs up to 0.2 km AGL | 28 days in the periods March-May and November-February from 2000 to 2004. Two to eleven measurements per day. | Effect of O₃ in the residual layer on the daily maximum O₃ concentration. |
| MILAGRO-INTEX-B | Ozonesonde | 35 km AGL | O₃, T, and RH | 7-13 March 2006, and 22 August-20 September 2006. One measurement per day around 13:00 LST | Long-range transport of O₃ in the North American region, and influence of stratospheric O₃ on the MCMA region |
| MILAGRO-2006 | Free-floating altitude-controlled meteorological balloons (CMET), and aircraft | 6 km ASL (CMET) | WS, WD, T, and RH | 7-22 March 2006, around 10:00 LST | Long-range transport in the residual layer (vertical mixing and horizontal dispersion of the MCMA plume) |
MCMA-2003 field campaign). During MILAGRO-2006 and IMADA-AVER (conducted in 1997) field campaigns, the diurnal growth of the ML was determined by various instruments in spring. Shaw et al. (2007) compared the differences in the ML evolution of these campaigns and found that, in the mid-to-late afternoon in MILAGRO, the ML was somewhat deeper than that in IMADA-AVER campaign. Note that the diurnal evolution of the ML in the MCMA is not evaluated by routine radiosonde measurements because they are launched at 6:00 and 18:00 local standard time (LST). It is important to remark that after the MILAGRO field campaign in 2006, no other observation of the O3 vertical distribution has been carried out in the MCMA until our field campaigns in 2011 and 2012.

Based on the past researches, various countermeasures against the air pollution have been implemented in the MCMA (SMA-GDF, 2012), resulting in rapid decrease of the annual mean O3 concentration until around 2000 and almost constant gradual decrease in recent years although large fluctuations occurred in some years. According to official emission inventories, emission rates of O3 precursors such as volatile organic compounds (VOCs) and nitrogen oxides (NOx) increased considerably from 2004 (VOCs: 532.2 kton year\(^{-1}\); NOx: 180 kton year\(^{-1}\)) to 2010 (VOCs: 602.4 kton year\(^{-1}\); NOx: 214.8 kton year\(^{-1}\)) by 13% and 19%, respectively (SMA-GDF, 2004; SMA-GDF, 2012). However, with the emissions inventories of O3 precursors such as NOx and VOCs still having many problems in accuracy and considering the nonlinear nature of O3 production where reduction of a precursor substance does not necessarily lead to decrease of O3, continued observation of O3 is necessary. Particularly, vertical profile measurement is important because O3 is produced in the atmosphere by photochemical reaction, transported by horizontal and vertical air flows, and destroyed by chemical reaction in the atmosphere and decomposition on solid surfaces.

Various aspects of the vertical structure of air pollution has been clarified by the previous studies, but a critical question still remains unanswered on how O3 is produced and distributed in the atmospheric boundary layer. In Velasco et al. (2008), vertical profiles of ozone up to about 1 km above the ground level (AGL) were measured using a tethered balloon at relatively short time intervals (≥70 min). However, windy conditions often limited the top height, and the diurnal cycle of ML, which grows as thick as 3 km on clear-sky days, let alone ozone profile could not be obtained through a course of a day. Their study, therefore, focused on the diurnal variation averaged over multiple observation days, and the influence of a particular meteorological condition was left unclear. In Thompson et al. (2009), ozonesonde was employed to obtain the vertical profiles up to the stratosphere. However, because their primary concern was the long-range transport of ozone in the upper-troposphere and the stratosphere, the ozonesondes were launched just once a day. Hence, profiles through ML were obtained but evolution during a day was not. In the present study, ozonesonde measurements were carried out twice daily, one in the morning and the other in the afternoon, to clarify the production and vertical redistribution of O3 in the ML. The ML heights during our observation days were determined from the vertical profiles of temperature by radiosonde using the Holzworth method (Holzworth, 1964).

The ozonesonde measurements are part of a more comprehensive field study including measurements of VOCs and PM\(_{2.5}\) (particulate matter with aerodynamic diameter less than 2.5 micrometers). Intensive field campaigns were conducted in a dry-cold (November 2011) and dry-warm (March 2012) seasons in Mexico City. We describe how meteorological condition affects the development of the vertical profile of O3. A good understanding of three-dimensional structure and life cycle of O3 will contribute to proposals of new action plans to reduce the O3 concentration in the MCMA.

2. STUDY AREA

The MCMA is located on a high plateau above 2000 m above sea level (ASL) in the central part of Mexico (Fig. 1). The MCMA consists of the Distrito Federal (DF), 59 municipalities from the Mexico State, and 1 municipality from the Hidalgo State. The MCMA has a population of more than 20 million, more than 5 million vehicles, and about 78,000 industries (CONAPO, 2012; SMA-GDF, 2012). The MCMA is surrounded by mountain chains reaching as high as 5,426 m ASL, with a wide and a narrow opening in the north and southeast, respectively.

Because natural convection from the heated plateau generates updraft, the wind comes predominantly from the north opening where adiabatically expanded cool air enters from the lower altitudes outside the MCMA, whereas often in the evening, strong wind enters from the narrow gap in the south-east (Molina et al., 2007). Although the wind near the ground has a relatively simple characteristic, the wind profile up to the height of the surrounding mountain tops (almost coincident with the top of the daily maximum ML) is highly variable because of the relatively small wind speed due to terrain shielding (de Foy et al., 2006).

Because of the high altitude and low latitude, the
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MCMA receives relatively strong ultraviolet radiation that promotes photochemical reaction to generate \( \text{O}_3 \) from precursor substances such as NO\(_x\) and VOCs.

Another important characteristic of the MCMA is the high emission rates of pollutants. Table 2 compares emission rates of representative pollutants in the MCMA, Distrito Federal (located in the core of MCMA), Tokyo, and Kanto area in Japan. Emission of CO in 2008 in the MCMA is more than twice higher than that in Kanto area in 2000, and emission rates of NO\(_x\) and VOCs were 2.6 and 5.7 times, respectively, higher than those from Tokyo, which has much less population (about 13 million) than the MCMA.

### Table 2. Mexican and Japanese rates of emission (kton/year) of representative pollutants.

|                | MCMA\(^1\) | Distrito Federal\(^1\) | Kanto area\(^2\) | Tokyo\(^3\) |
|----------------|-------------|-------------------------|------------------|-------------|
| Area (km\(^2\)) | 7,866       | 1,485                   | 32,385           | 2,187       |
| PM\(_{10}\)     | 16          | 4                       | 32,385           | 2,187       |
| PM\(_{2.5}\)    | 11          | 3                       | 30               | 3.2         |
| SO\(_2\)        | 8           | 3                       | 153              | 8.1*        |
| CO              | 2,697       | 1,092                   | 1,330            |             |
| NO\(_x\)        | 309         | 157                     | 589              | 68.8        |
| VOCs            | 571         | 264                     | 854              | 100.8       |
| NH\(_3\)        | 42          | 19                      | 6.1              |             |

\(^1\)SEMARNAT, 2015. Base year 2008
\(^2\)WMO-IGAC, 2012. Base year 2000
\(^3\)Tokyo Metropolitan Research Institute for Environmental Protection, 2011. Base year 2008

*Navigation occupies 5.8 kton/year

### 3. OBSERVATION METHODS

On 17, 22, and 23 November 2011, and 7, 8, 9, 12, 13, and 14 March 2012, balloon-borne measurements were conducted in the MCMA. The balloon launch site was the rooftop of the Mexican National Weather Service (SMN) building (19°24′13″N, 99°11′46″W, 2313 m ASL; see Fig. 2) where routine atmospheric soundings are conducted twice daily at 06:00 LST and 18:00 LST.

The instruments used were GPS radiosonde (Meisei Electric, Japan) for obtaining meteorological parameters (T, RH, WS, and WD) and ozonesonde (GPS radiosonde attached to an electrochemical concentration cell (ECC) \( \text{O}_3 \) sensor made by EnSci Co., U.S.A.). A GPS radiosonde was launched at 08:30 and 17:00 LST, and an ozonesonde was launched at 11:30 and
14:30 LST. The instruments ascended at about 5 ms⁻¹ up to about 16 km ASL for radiosonde and to about 30 km ASL for ozonesonde until the balloon burst. As described in Kanda et al. (2014), the ozonesonde was interfered occasionally by SO₂ plumes in MCMA. The interference events are excluded in our analysis.

During both field campaigns, O₃ concentration at the surface level was recorded by a UV absorption O₃ monitor (OA-781, Kimoto Electric, Japan). The monitor was calibrated by a dynamic dilution calibrator Teledyne API, Model 700 against the Standard Reference Photometer #39. The MCMA has an air-quality monitoring network of 38 stations, of which 23 measures O₃. Figure 2a and 2b show the distributions of 1-h average O₃ concentrations on 8 March 2012 for 10:00-11:00 LST and 13:00-14:00 LST, respectively. The highest O₃ concentration in our field campaigns was recorded on this day. We observe broadly distributed area of high O₃ concentration in the afternoon.

**Fig. 2.** Distributions of 1-h average O₃ concentrations (ppbv) on 8 March 2012 prior to 11:00 LST (a) and 14:00 LST (b), measured by the automatic air quality monitoring network (RAMA) of the MCMA. (c) Distribution of population density (inhabitants km⁻²) in the urban area of the MCMA and surroundings. The area considered for estimation of O₃ production is enclosed by a dark blue line.
4. RESULTS AND DISCUSSION

4.1 Results of Observations above the Mixing Layer

We present the whole vertical profiles of $O_3$, and show the validity of the measurements. Figure 3 shows the observed profiles of $O_3$ partial pressure ($P_{O_3}$) up to 30 km ASL for the 14:30 LST launches. In ML, $P_{O_3}$ increases because of photochemical production involving anthropogenic NO and VOCs, and becomes approximately uniform vertically due to convective mixing. During our observation campaigns, tropopause was found around 15 km ASL. The growing maximum of $O_3$ concentration around 13 km ASL from 13 March 2012 can be attributed to stratospheric influence as described by Danielsen (1968) and Thompson et al. (2008).

In the upper troposphere (8-17 km ASL), $P_{O_3}$ was lower in November 2011 (0.4-1.6 mPa) than in March 2012 (1.0-2.2 mPa), a seasonal variation consistent with previous observations. The higher upper-troposphere concentration in March than in November can be attributed to increased intrusion from stratosphere (Singh et al., 1978; Danielsen, 1968), increased biomass burning and the resulting emission of carbon monoxide (Ou Yang et al., 2012; Penkett et al., 1998), or increased solar radiation working on precursor substances accumulated during winter. It is, however, not certain which factor contributed most in the sub-tropical region of Mexico. In the stratosphere (> 15 km ASL), maximum $P_{O_3}$ (12 to 16 mPa) was observed in the ozone layer around 26 km ASL, with little difference between November and March.

4.2 Meteorological Conditions and Temporal Variation of Surface $O_3$ Concentration

Figure 4 shows the vertical profiles of the meteorological parameters and $O_3$ concentration for two representative days in the November 2011 and March 2012 campaigns. The November 2011 campaign belonged to the change of seasons from wet to dry-cold. The prevailing wind direction in the upper troposphere was west on 17 November 2011 typical of the dry-cold season (Fig. 4a), but was east on 22 and 23 November 2011 typical of the wet season. During the March 2012 campaign, the upper-tropospheric wind was consistently from the west, indicating that the dry season had settled in.

The wind direction in ML was north-northeast-east during the November 2011 campaign, highly variable on 7 and 8 March 2012, and north to northeast for the rest of the March 2012 campaign (not shown). As described below, the change of wind pattern on 9 March 2012 preceded the arrival of a cold surge and the low levels of $O_3$ concentration on the following days. Figure 5a shows the diurnal evolution of the ML height determined for all the observation days by the Holz-
Fig. 4. Vertical profiles of meteorological parameters and O₃ concentrations at 11:30 and 14:30 LST on 17 (a) and 22 November 2011 (b) and 8 March 2012 (c). Black horizontal lines indicate the ML height.
worth method (Holzworth, 1964). Data at 06:00 LST were obtained from the regular radiosonde measurements at SMN. Furthermore, Figure 5b shows the ventilation coefficient (VC) calculated as the product of the ML height and the mean wind speed in the ML (Athanassiadis et al., 2002). VC is a measure of the dilution efficiency of the atmospheric boundary layer and is useful for analyzing the dispersion and accumulation of air pollutants near the surface (Haman et al., 2014; Athanassiadis et al., 2002).

Because observation days in March 2012 had clearer sky than those in November 2011, the early morning surface inversion and the rapid heating of the ground resulted in initially slower but later faster growth of the ML height. Our observation is consistent with Velasco et al. (2008) who by tethered-balloon measurement confirmed rapid growth of ML height around 8:00-9:00 LST and saturation after around 14:00 LST. Athanassiadis et al. (2002) found that VC was relatively low in the morning and high in the afternoon on days with high daily maximum O₃ concentration in the summer of 1997 in Philadelphia, USA. This observation implies that, on a high-O₃ day, typically a clear-sky day under the influence of a high-pressure system, wind speed is low and ML is thin in the morning due to surface inversion, and wind speed is high and ML is thick in the afternoon due to intense solar radiation and vertical mixing. In our study, if the periods of November 2011 and March 2012 are compared, the mean VC at 11:30 LST of November 2011 was about 28% larger than that of March 2012, whereas the mean VC at 14:30 LST of November 2011 was 29% lower than that of March 2012. Because O₃ concentration was higher in March 2012 than in November 2011, our observation is consistent with that of Athanassiadis et al. (2002).

Figure 6 shows the temporal variations of O₃, NOₓ, and CO concentrations, and WS and temperature at surface. NOₓ and CO are good indicators of traffic emission. For those days and those pollutants that were not measured at the SMN site, data from the air monitoring station Pedregal (PED, located around 8.7 km to the south of the SMN) from the automatic air quality monitoring network (RAMA by Spanish acronym) were used. On each day, concentration of O₃ was lowest early morning because of continued destruction on solid surfaces from the previous night and titration by nitric oxide (NO) emitted from the rush-hour traffic of the previous evening and the morning of the day when the concentration was increased by the surface temperature inversion. As sunlight intensified, VOCs and NOₓ emitted by human activity generate O₃ by photolysis, and the highest concentration occurred late in the afternoon.

On the ozonesonde launching days in the November 2011 campaign (Fig. 6a), O₃ concentration was relatively low due to cloudy weather and low temperatures. Relatively high O₃ concentrations were recorded over the weekend of 19, 20, and 21 November 2011 (21 was a national holiday) due to the high temperature and probably to the “weekend effect” (Garcia-Reynoso, 2009) where less emission of NO results in less titration of O₃ and higher ratio of VOCs/NOₓ leads to rapid O₃ production.

The first week of the March 2012 campaign was relatively warm with the highest O₃ concentration on 8 March 2012 (Fig. 6b). Over the weekend of 10 and 11 March 2012, a cold surge arrived from the north resulting in unusually low temperature culminating in a
strong hail in the afternoon of 10 March 2012. The second week was relatively cool with occasional rain in the evening resulting in the O$_3$ concentration decreasing day by day.

4. 3 Ozone Vertical Distribution

Vertical profiles of O$_3$ concentration up to 6 km are shown in Figure 7. Around 5 km ASL in November 2011 campaign and near the ground for the 11:30 LST...
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launch on 14 March 2012 (the ground-level O₃ concentration by a UV-absorption monitor was about 50 ppbv whereas the ozonesonde output was about 30 ppbv; the difference was approximately the same as the SO₂ concentration measured by a UV-absorption monitor at SMN), abnormal decreases in the ECC sen-

Fig. 7. Vertical distributions of O₃ up to 6 km ASL.
sor signal were recorded. As described in Kanda et al. (2014), these decreases are attributed to the interference by SO2 plumes from Popocatepetl volcano in the case of November 2011 and from the northern industries in the case of 14 March 2012.

O3 concentration in ML increased considerably from the morning to the afternoon due to photochemical production. Relatively low production was observed on 17 November 2011 although the O3 concentration level at 11:30 LST at the surface was relatively high. The high concentration at 11:30 LST is attributable to the relatively strong low-level wind (about 5 m s⁻¹ at 140 m AGL) and the resulting down-mixing of the high O3 concentration air-mass in the residual layer. The low production is due to the cloudy weather as represented by the low temperature.

### 4.4 Production of Ozone in Mexico City

O3 produced in the ML between the 11:30 and 14:30 LST was estimated as follows. It was assumed that O3 produced near the ground was distributed and confined in ML above a selected region of MCMA. A region was selected based on the population density. Because most of the air pollutants are released from anthropogenic activities, we considered that high population density indicated high pollutant emissions. Therefore, based on the most recent census 2010 from the National Institute of Statistics and Geography of Mexico (INEGI by Spanish acronym), urban areas with high population density (> 3000 inhabitants km⁻²) located in the core of the MCMA with average elevation of around 2.4 km ASL, were selected (Fig. 2c). Horizontal transport across this region was not considered. The vertical profile of P03 over the selected region was assumed identical. Then, the O3 increase (∆QO3) between the 11:30 and 14:30 LST can be calculated by

\[
Q_{O3}(t) = A \int_{z_S}^{z_m} C_{dz} = A \sum_i \frac{C_i + C_{i+1}}{2} (z_{i+1} - z_i) \tag{1}
\]

\[
\Delta Q_{O3} = Q_{O3}(t_2) - Q_{O3}(t_1) \tag{2}
\]

where QO3(t) is the O3 amount at time t, A (equal to 872 km²) is the area of the selected region (dark blue contour in Fig. 2c), Ci is the mass concentration of O3, z_S and z_m are the ASL height of the ground and the top of ML at 14:30 LST, respectively, and t_1 and t_2 represent 11:30 LST and 14:30 LST, respectively. Multiplication by the area A is done for direct comparison with numerical simulation by a chemical transport model, which will be published elsewhere. Because there were no particular local maxima of O3 concentration above ML, the increase ∆QO3 can be regarded as due to photochemical production. The calculated ∆QO3 are shown in Table 3. The case of 14 March 2012 was excluded because the measurement at 11:30 LST was interfered considerably by SO2 plume in ML (Kanda et al., 2014).

| Date               | ∆QO3 (ton) |
|--------------------|------------|
| 17 November 2011   | 28         |
| 22 November 2011   | 65         |
| 23 November 2011   | 62         |
| 07 March 2012      | 105        |
| 08 March 2012      | 247        |
| 09 March 2012      | 60         |
| 12 March 2012      | 94         |
| 13 March 2012      | 73         |

### Table 3. Production of O3 from 11:30 to 14:30 LST over the selected region in MCMA estimated from ozonesonde measurement data.

Previous studies (Wakamatsu et al., 1995; Davidson, 1993) show that the number of days in a given period with daily maximum hourly-average concentration of ground-level O3 exceeding 120 ppb is positively correlated with the average of the daily maximum temperature in the same period. Figure 8a shows a scatter plot between ∆QO3 and the daily maximum hourly-averaged temperature. We observe fairly good positive correlation. As discussed in Sect. 4.2, diurnal variation of VC influences the production and dilution of O3. Figure 8b is a scatter plot between ∆QO3 and the ratio of VC in the afternoon (14:30 LST) to that in the morning (11:30 LST). We observe approximately positive correlation, which is consistent with the results of Athanassiadis et al. (2002) and Haman et al. (2014). In the following, we discuss three cases that appear to deviate from the correlation lines.

On 17 November 2011, the lowest ∆QO3 among all the observation days occurred. On this day, the concentration of O3 was relatively high at 11:30 because of the cloudy and windy (2.9 m s⁻¹ at surface at 6:00 LST) weather in the morning and the consequent down-mixing of the high O3 air-mass in the residual layer left from the previous day when the daily maximum O3 concentration was above 100 ppb at PED station (Fig. 6a). However, the continued cloudy weather and the consequent low temperature restricted photochemical production.

On 8 March 2012, when the highest ∆QO3 among all the observation days occurred; ∆QO3 was larger by more than twice than that on the previous day (7 March 2012) even though the daytime temperature was approximately the same. A factor that led to the high ∆QO3 on 8 March 2012 is the large VC ratio as shown in Fig. 8b. The ML growth rate from 8:30 to 11:30 (297 m h⁻¹) was around 60% lower than on the previous day and the VC (2,877 m² s⁻¹) before noon
was the lowest among all the observation days. In the afternoon when the surface was warmer and the WS increased, a larger VC was recorded (15,293 m$^2$ s$^{-1}$) accompanying the increase in the ML growth rate (500 m h$^{-1}$). The low VC in the morning and high VC in the afternoon are indications of high daily maximum O$_3$. An additional difference between 7 and 8 March 2012 was the trajectory of the air mass. Figure 9 shows the horizontal trajectories of the observation balloons from the ground to a little above the top of ML indicated by crosses. We observe that the travel distance up to the top of ML was particularly short at 11:30 on 8 March 2012. Moreover, as Figure 9 shows, there was a reversal in the wind direction in ML, and the distance from the launching site to the location where the balloon reached the top of the ML for the launch at 14:30 LST was shorter than 500 m. Therefore, the ML was relatively stagnant, which may have promoted the storage of O$_3$ and its precursors in the ML.

On 9 March 2012, $\Delta Q_{O_3}$ was relatively low despite the high daily maximum temperature and the large VC ratio. Clear evidence cannot be provided for this case, but the following circumstances may be noted. Firstly, $\Delta Q_{O_3}$ on this day could have been an underestimate because, as shown in Figure 6, the ground level O$_3$ was past the daily peak when the ozonesonde was launched. Secondly, the afternoon ozonesonde launch was immediately before the arrival of a cold surge as indicated by the sudden increase in RH and WS and decrease in T. Hence, there could have been intrusion.

**Fig. 8.** Relationship between $\Delta Q_{O_3}$ and (a) daily maximum hourly-averaged surface temperature and (b) ratio of VC in the afternoon (14:30 LST) to that in the morning (11:30 LST) in the MCMA during the November 2011 and March 2012 field campaigns. Black square symbols were exceptional cases and are not considered in the linear regression.

**Fig. 9.** Horizontal trajectories of the observation balloons on 7, 8, and 9 March 2012 at (a) 11:30 LST and (b) 14:30 LST. The coordinate origin represents the launching site SMN, and crosses indicate the locations where the balloon reached the top of ML.
of low-O₃ air-mass from outside of the MCMA possibly in the upper part of ML.

5. CONCLUSIONS

Vertical profiles of O₃ concentration over the MCMA were investigated using ozonesonde launched twice daily at 11:30 LST and 14:30 LST in field campaigns in November 2011 and March 2012. O₃ produced near the ground was observed to be distributed approximately uniformly in ML.

The observation days in November 2011 were characterized by cloudy weather, wind patterns favorable for the dispersion of pollutants and wind directions in the upper troposphere typical of the transition from wet to dry-cold season. Under the warmer weather condition during the observation days in March 2012, the following diurnal pattern was clearly observed: thermal inversions at surface level occurred in the morning, rapid heating of the ground followed, and the ML height grew relatively fast after the MCMA rush hours (8-9 LST).

In the first week of the March-2012 campaign, relatively high temperature was recorded as well as high O₃ concentration. During the weekend of 10-11 March 2012, a cold surge arrived from the north of the MCMA producing a decrease in the temperature. The next weekdays were relatively cool and occasional rain was observed in the evening, with decreasing O₃ concentrations.

The ML height and VC were estimated from the meteorological data. O₃ produced and stored (∆Q₀₃) in ML between 11:30 LST and 14:30 LST was estimated from the vertical profiles obtained by ozonesonde. The magnitude of ∆Q₀₃ was confirmed to be positively correlated with the daily maximum temperature for most of the observation days.

This study confirmed the importance of vertical sounding of the atmosphere. Especially, the significance of frequent and deep soundings should be emphasized; the twice-daily ozonesonde observations through and beyond the mixing layer enabled estimation of the amount of photochemically produced ozone, and the four-times-daily radiosonde observations helped identify the causes for the behaviors where the ∆Q₀₃ - T_max relation was exceptional. In the past studies, similar analysis could not be conducted because the vertical soundings were either frequent but shallow (tethered balloons; Velasco et al., 2008), or deep but infrequent (once-or-less-daily ozonesonde; Thompson et al., 2008).

The observation results will be useful for validating atmospheric transport models in future work, and will contribute to proposals of efficient countermeasures to photochemical air pollution in the MCMA.

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