Vertical Profile of Ozone and Accompanying Air Pollutant Concentrations Observed at a Downwind Foothill Site of Industrial and Urban Areas

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ABSTRACT

This study measured vertical distributions of ozone, sulfur dioxide, nitrogen oxide, carbon monoxide, six biogenic-related volatile organic compounds, wind vector, humidity and temperature within the Planetary Boundary Layer (PBL) below 1200 m using a tethered balloon sounding system at a downwind rural site in the Taichung Basin, Taiwan, during the 2002 summer. During ozone episodes, both nocturnal inversion and valley-mountain wind circulation were stronger than those during non-episode days. The observed vertical distributions of these pollutants indicate that the concentrations of carbon monoxide, nitrogen monoxide and biogenic volatile organic compounds decreased as the height increased. Conversely, the highest ozone concentrations were measured during early afternoon at heights of 100-600 m above ground level. Notably, these high ozone concentrations were normally accompanied by relatively higher concentrations of nitrogen dioxide and sulfur dioxide, but not carbon monoxide. From emission inventory, trajectory analysis and statistical analysis, all suggest that high-stack point sources have an important role in causing the summer ozone episodes. This suggestion is supported by 11-y summer data at three stations in the Basin. In addition, it is found that part of the early-afternoon surface ozone was from ozone stored aloft in the residue layer at heights above the nocturnal boundary layer of the preceding night.

Keywords: Tethersonde system; Ozone; Vertical profile; Nocturnal inversion; Valley-mountain wind circulation.

INTRODUCTION

Based on data for the recent decade in central Taiwan, the worst ozone episodes typically occur during autumn and spring (Taiwan EPA, 2003). Nonetheless, summer ozone episodes began monitored since 2002. This study presents the first field campaign data obtained in summer, when a few high ozone episodes occurred. Central Taiwan is of particular interest for air-quality studies, as this region is home to the Taichung Power Plant (TP) and Mailiao Power Plant (MP) (Fig. 1). The TP became operational in 1991, followed by MP in 2001. The TP and MP ranked first and sixth worldwide in terms of the amount of CO2 they emit, respectively (Tollefson, 2007).

Data for ozone (O₃), sulfur dioxide (SO₂), nitrogen oxide (NOₓ), carbon monoxide (CO), methane (CH₄) and non-methane hydrocarbon (NMHC) concentrations were routinely obtained by Taiwan Environmental Protection Administration (EPA) via its air-quality monitoring network in central Taiwan. Although pollutant sources in urban or industrialized areas generate the most pollution, poor air quality is frequently encountered in downwind rural areas (Comrie, 1994; Stibello et al., 1998; Debaje and Kakade, 2006; Kumar et al., 2008; Yang et al., 2008; Yang et al., 2008). In particular, ozone and secondary PM₂.₅, typically produced in 30-200 km downwind of precursors NMHCs, NOₓ and SO₂ (MacKenzie et al., 1995; Lin et al., 2008; Kuo et al., 2009), are photochemically formed under stagnant meteorological conditions (Oke, 1987; Aneja et al., 1994; Vukovich, 1994; Ludwig et al., 1995; Seinfeld, 1998; Cheng, 2001; Cheng et al., 2001; Devara et al., 2005; Hung et al., 2005; Wang and Chen, 2008).

Recent studies demonstrated that ozone and its precursors can be stored aloft during the night and mixing downward towards the ground when the ground surface heats up and the nocturnal inversion breaks up in the morning (McElroy and Smith, 1986; Padro et al., 1991; Neu et al., 1994; Dayan and Koch, 1996; McKendry et al., 1997; Pisano et al., 1997; Güsten et al., 1998; Lehning et al., 1998; Seibert et al., 2000; Chen et al., 2002; Lin et al., 2007; Lin, 2008). Vertical distributions of ozone and ozone precursors, such as NO, CO and volatile organic compounds (VOCs), were investigated in a few field studies at other locations (Anlauf et al., 1994; Bottenheim et al., 1997; Güsten et al., 1997; Hayden et al., 1997; Helmis et al., 1997; Pisano et al., 1997; Güsten et al., 1998; Greenberg et al., 1999; Chen et al., 2002; Lin et al., 2004; Tsai and Tsuang, 2005; Tseng et al., 2009). Such data helps in describing dry deposition and removal processes of O₃, explaining the causes of high pollution events (Colbeck and Harrison, 1985), and providing input for initialization, testing and development of atmospheric chemistry models (Hoff et al., 1995; Hedley and Singleton, 1997). These data can also be utilized to supply the basic scientific information for clean air strategies (Baumbach and Vogt, 1999).

This study used a tethered balloon to acquire the vertical and temporal distributions of airborne pollutant concentrations and meteorological variables to a height of 1200 m at a rural site in Caotun (120°39′29.1″ E, 23°59′12.1″ N), and 110 m above sea level (ASL) (Fig. 1). The site is located in the foothills of the Taichung Basin, where the pollutant such as ozone was transported (Taiwan EPA, 2003; Chen et al., 2002). This study focused on the major species O₃, CO, SO₂, NO, NO₂ and six VOCs (Isoprene, methacrolein (MACR), methyl vinyl ketone (MVK), limonene, α-pinene and β-pinene) during the summer field campaign in 2002. The relationships of the ozone
concentration with accompanying pollutants and meteorological conditions are studied. Trajectories and likely reasons for causing the ozone episodes at the foothill site are presented.

DESCRIPTION OF THE STUDY SITE AND FIELD CAMPAIGNS

The field study ran from Aug. 11th-26th, 2002. During this campaign, vertical pollutant concentration profiles and meteorological data were recorded at 3-h intervals—00, 03, 06, 09, 12, 15, 18, 21 Local Time (LT)—except when under the conditions of rain, strong wind (wind speed > 10 m/s) or instrument malfunction, such that during a power failure. The major pollution sources upwind of the study site are local traffic, Taichung City and industrial areas located along the coast. The traffic volume along nearby Express road way 63 was measured on Aug. 29th, 2001. Fig. 2 shows the emission rates for CO, NOx and SO2 from the expressway based on traffic volume data. High traffic flow during 7-21 LT on weekdays generated higher CO and NOx emissions than those during other hours. The CO emission rate was highest, followed by those for NOx and SO2.

Table 1 lists the emission rates of CO, NOx and SO2 from point, line and area sources in the study region (CTCI, 2000). The dry deposition rates and the chemical decay rates for CO, SO2, NO and NO2 over land (Hertel et al., 1995, Tsuang, 2003; Tsuang et al., 2003) are also shown in the table. Vertical profiles of meteorological variables were recorded at 5-1200 m above ground level (agl) using a tethersonde system (Atmospheric Instrumentation Research, Inc., U.S.A) which measures temperature, specific humidity, pressure and wind vector. The tethersonde system consists of a balloon with a buoyancy of roughly 9.3 kg, an AIR-TS-3AW winch with tether, an IS-5A-RCR, 403 MHz receiver with a preamp and antenna, laptop computer and a TS-4A-SP-403 tunable sensor package. Balloon height was determined from pressure variations measured by the tethersonde system (Fig. 3).

Vertical distributions of CO, SO2, NO, NO2 and O3 were also determined by the tethersonde system. A specially designed lightweight (600 g) sampling pump with a timer was utilized to...
Table 1. Emission, dry deposition rate and chemical decay rate of CO, SO\textsubscript{x} and NO\textsubscript{x} in the region of 23.5 N to 24.8 N and 120.1 E to 121.3 E.

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>SO\textsubscript{x}</th>
<th>NO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point sources</td>
<td>39,522  (16)</td>
<td>54,963   (92)</td>
<td>89,849   (57)</td>
</tr>
<tr>
<td>Line sources</td>
<td>179,965 (73)</td>
<td>1,502     (3)</td>
<td>59,024   (38)</td>
</tr>
<tr>
<td>Area sources</td>
<td>27,838 (11)</td>
<td>3,014     (5)</td>
<td>8,335   (05)</td>
</tr>
<tr>
<td>Total</td>
<td>247,325 (100)</td>
<td>59,478    (100)</td>
<td>157,208 (100)</td>
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<th></th>
<th>CO</th>
<th>SO\textsubscript{2}</th>
<th>NO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taichung Power Plant</td>
<td>0</td>
<td>11,706   (20)</td>
<td>31,862   (20)</td>
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<table>
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<tr>
<th></th>
<th>CO</th>
<th>SO\textsubscript{x}</th>
<th>NO\textsubscript{x}</th>
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</thead>
<tbody>
<tr>
<td>Dry deposition rate (cm/s)\textsuperscript{b}</td>
<td>0.01</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Chemical decay rate (%/h)\textsuperscript{c}</td>
<td>0</td>
<td>7.8</td>
<td>0.75</td>
</tr>
</tbody>
</table>


Fig. 3. Schematic diagram for the tethered balloon sampling apparatus used in the field campaign.

Due to the payload limit of a tethersonde system, the vertical and temporal concentration distributions of six VOCs species (isoprene, MACR, MVK, limonene, α-pinene and β-pinene) were sampled using another tethersonde system during daytime (9-18 LT) on Aug. 14\textsuperscript{th}-17\textsuperscript{th}, 2002. These biogenic VOCs were sampled at heights of 2, 10, 100, 200, 400, 600 and 800 m. The sampling instrument had an ozone filter, adsorbent tube, sampling pump and Teflon sampling bag (Fig. 3); Teflon was utilized as the connecting pipeline. An ozone filter was located at the entrance of the gas inlet to eliminate any reactions between ozone and the sample. An adsorbent tube was connected to the ozone filter, and was filled with absorbent Tenax-TA, a porous polymer containing 2, 6-diphenyl-p-phenylene. The Teflon sampling bag and cartridges were installed at the gas outlet for sample collection. The collected samples were analyzed using gas chromatography with a flame ionization detector (FID), a similar procedure to that described by Greenberg \textit{et al.} (1999).
Furthermore, three standard air-quality monitoring stations are located near this study site (Caotun (Fig. 1), two of which are operated by Taiwan’s EPA, that at Dali (120°40'40.0" E, 24°05'58.1" N) and Nantou (120°41'23.1" E, 23°58'49.5" N) was operated by the Taiwan Power Company. Additionally, a photochemical assessment monitoring station (PAMS) near Caotun (120°41'18.5" E, 23°58'44.9" N) was operated by Taiwan’s EPA. At the PAMS, concentrations of 55 VOCs species were measured by the Taiwan Power Company. Additionally, a photochemical assessment monitoring station (PAMS) near Caotun during the day and southern wind during night was stronger on period days than that on non-period days. The same wind patterns were also observed at the nearby Caotun station (Fig. 5). During episodes, wind speed at about 600-800 m agl was relatively slow compared to that at heights < 600 m agl. Below 400 m, synoptic wind and mountain wind during episodes came from the south, this southern wind prevailed until 11 LT. The wind then shifted to the north (valley breeze) and lasted until 19 LT. During non-episodes, valley-mountain wind circulation was much weaker and the wind system was controlled by a southwest monsoon. In summer during daylight hours, a northern wind was dominant during episodes, whereas a western wind was dominant during non-episodes (Figs. 5 and 6(a)). At nighttime, a southern wind was dominant during episodes and non-episodes.

The change in the wind direction was accompanied by a change in humidity. During episodes when a valley wind was dominant, specific humidity was roughly 22 g/kg, but decreased to 19 g/kg when a mountain wind was dominant. This is reasonable because downhill wind is generally drier than uphill wind. During non-episodes, specific humidity remained almost constant at approximately 20 g/kg during day and night.

The daily mixing height in ozone episode days were apparently lower than the non-episodic days (Fig. 6). Moreover, the air was more stable during episodes than during non-episodes. During night, the potential temperature gradient at < 100 m was 0.01 K/m during episodes and 0.005 K/m during non-episodes. Thus, the nocturnal inversion was much stronger during episodes than during non-episodes. After sunrise, vertical mixing started at the ground surface and grew to a maximum of roughly 600-800 m in the afternoon during episodes, and > 1000 m during non-episodes.

**RESULTS**

In total, 107 profile samples were collected and analyzed. Figs. 4-7 shows analytical results. The Pollutant Standard Index (PSI) was used to describe air quality and when the PSI exceeded 100, air quality was unhealthy. The PSI was 100, resulting from a maximum hourly ozone concentration of 120 ppb. Therefore, this study used the ozone concentration for the PSI to define episode periods and non-episode periods. Fig. 4(a) shows the maximum ozone concentration of every vertical profile. The index is 120 ppb. During Aug. 16th-18th, it takes three days in succession and the ozone concentration exceeded 120 ppb, whereas during Aug. 23rd and 25th it did not. Figs. 4(b) and (c) show a similar pattern for ozone concentration at the two EPA stations and study data on surface and at 100 m. Moreover, the time series of other pollutants, such as NO and SO2, and meteorological conditions had different phenomena in two different periods (Figs. 4(e)-(i) and 4). Therefore, this study denotes the period of Aug. 16th-18th as an ozone episode, and the period of Aug. 23rd and 25th as a non-episode.

**Meteorological Conditions**

Fig. 5 shows the time series of meteorological variables observed at this study site and nearby stations. Typical diurnal patterns of vertical profiles of potential temperature, wind field and specific humidity were observed at the study site during the episode on Aug. 18th and the non-episode on Aug. 25th (Fig. 6). The wind patterns during episodes and non-episodes differ. The valley-mountain wind circulation that resulted in a northern wind during the day and southern wind during night was stronger on episode days than that on non-episode days. The same wind patterns were also observed at the nearby Caotun station (Fig. 5).

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**CO, SO2, NO and NO2 Profiles**

Fig. 7 shows the vertical profiles of CO, SO2, NO (primary pollutants) and NO2 (secondary pollutant) during episode days and non-episode days, respectively. The concentration ranges of CO, SO2, NO and NO2 profiles were approximately 0.6-0.9 ppm, 2-7 ppb, 1-5 ppb and 10-30 ppb, respectively. Table 1 shows that CO had a high emission rate, slow dry deposition velocity and slow chemical-decay rate (Table 1). Moreover, CO is relatively inert; thus, CO has few opportunities to react with other chemical species. Above the nocturnal boundary layer (NBL), the CO concentration exceeded about 0.7 ppm during episodes, slightly higher than the value of 0.6 ppm during non-episodes. During episodes, which were usually under calm wind and stable conditions, the lifetimes of pollutants are much longer than during non-episodes (Tsunag and Chao, 1997; 1999).

In contrast, the chemical decay rates for SO2 and NO are significantly higher than that of CO. Both SO2 and NO rapidly reached a pseudo steady state, and converted to sulfate and NO2, respectively. The NO2 profiles are consistent with the fact that NO2 (NO + NO2) has the second longest emission rate (Fig. 2), and NO2 has the second slowest chemical decay rate. Interestingly, during episodes, peak concentrations of SO2 and
Fig. 4. The time series of pollutants concentration (a) the maximum ozone concentration of every vertical profile and the index is 120 ppb. (b) ozone for EPA station (Dali and Nanton). (c) ozone, (d) CO, (e) SO₂, (f) NO and (g) NO₂ for this field study on surface (2 m agl) and at 100 m agl; (h) NO₂ and (i) SO₂ for air quality monitoring stations (Caotun and Nanton).
Fig. 5. The time series of meteorological conditions, where (a) WD and (b) WS at this study site (100 m agl) and Caotun station respectively.

Fig. 6. Profiles of meteorological conditions on an episode (18th Aug., 2002) and a non-episode (25th Aug., 2002) at the study site, where the x-axis represents the local time (hour). (a) potential temperature, (b) specific humidity and (c)wind field.
Fig. 7. Composites of the profiles of CO, SO2, NO, NO2 and O3 on episodes (16th-18th Aug., 2002) and non-episodes (23rd and 25th Aug., 2002).

NO2 were typically found at 100 m agl at 15 LT; however, no such peaks were found for CO.

The vertical structure of profiles of the four pollutants vary greatly in the lower part of the PBL (< 70 m height) and remain almost constant above 200 m agl. The lowest part (< 10-20 m) is called the canopy layer (or deposition layer); the second lowest part (20-70 m height) is the inertial sub layer; and the upper part (70-1000 m) is the mixed layer (Stull, 1988). Within the inertial sub layer, vertical profile gradients for inert pollutants are controlled mainly by their vertical fluxes (Businger et al., 1971), which are functions of dry deposition and emission rates. In the mixed layer, all inert pollutants are considered well mixed. The profiles shown are consistent with an understanding of the vertical structure of PBL.

Ozone Profile

Fig. 7 presents ozone vertical profiles during episode days and non-episode days, respectively. These profiles demonstrate that...
O₃ concentrations decreased rapidly toward the ground. This is because surface O₃ was partly removed by deposition and reactions with NO at the surface. During episodes, concentrations at elevated levels were higher than those near the surface, reaching nearly 140 ppb at 100-300 m agl at noon and in the early afternoon. The time series of O₃ vertical profiles, the concentrations at all heights of vertical profiles increased from 9 to 15 LT and, then, returned to their original values in the afternoon, which swing like a pendulum (Chen et al., 2002). These concentration profiles indicate that photochemical production and convection were stronger at noon and early afternoon than later in the nightfall and evening. When stable nocturnal inversions formed and NO emissions increased in evening rush hours (roughly 18 LT) (Fig. 2), air masses were constrained in the NBL and ozone was rapidly depleted due to a continuous depletion process, and a relatively higher O₃ concentration was sustained above the NBL.

During non-episodes, pattern of O₃ vertical profiles and the time series resembled those during episodes. The concentration of O₃ at high altitudes was also higher than that at the surface and peak O₃ concentrations reached only around 90 ppb at 12-15 LT. Unlike the vertical profiles experienced during episodes, the ozone concentration decreased smoothly near the surface during non-episodes. During night, the elevated O₃ concentration had little effect on the emitted NO, which was confined within the NBL and, thus, preserved its high concentration.

Biogenic Related VOCs Profiles
Fig. 8 presents the biogenic VOCs vertical profiles. The VOCs concentrations were high at noon and in the early afternoon and relatively lower during morning and evening hours. Samples obtained near the surface had the greatest VOCs concentrations, which eventually decreased as the height increased. In particular, maximum concentrations of isoprene and its oxidized products (MACR and MVK) occurred at the surface and markedly decreased at heights up to 100 m. In contrast, the VOCs concentrations varied slightly above 100 m. The concentration gradients of isoprene and its oxidized products (MACR and MVK) profiles were approximately 0.2-1.8 ppb, 1-5 ppb and 2-18 ppb, respectively. The vertical profiles of limonene, α-pinene and β-pinene had a similar trend. Since the vertical profiles of the biogenic VOCs did not show peaks within 100-300 m agl, as observed in ozone profile in the early afternoon (Fig. 7), it is unlike for biogenic VOCs to be main precursor causing the ozone peaks within the 100-300 m agl height range.

DISCUSSION
Residual Ozone Layer and Downward Mixing Effect
When the atmospheric turbulence was strong in the afternoon, surface O₃ concentration reached the maximum and O₃ concentration at high altitude is also up to the maximum. The ozone at high altitude can remain above the mixing layer and NBL through to the next early morning and these O₃ will contribute to O₃ concentrations in the daytime next day. This layer is so-called residual ozone layer (Neu et al., 1994) and the phenomena have also been observed in Southern Taiwan (Lin et al., 2007; Lin, 2008). In this study, daily maximum mixed layer was about 750 m agl in the episode day and more than 1000 m agl in the non-episode day (Fig. 6). The result of the maximum mixed layer was about 750-1700 m agl during this field campaign. During episode days, the ozone concentration at 1000 m agl remained relatively high at night (Fig. 7). This phenomenon indicates that ozone and its precursors can be stored aloft during the night. Fig. 9 shows the correlations between O₃ concentrations at 100 m agl at 15 LT and O₃ concentrations above the NBL.

Fig. 8. Profiles of biogenic VOCs in the daytime (9LT–18LT) during 14th–17th Aug., 2002. (a) Isoprene, (b) Methacrolein (MACR), (c) Methyl vinyl ketone (MVK), (d) Limonene, (e) α-pinene and (f) β-pinene.
during the previous 9, 12, 15 h (06 LT, 03 LT, 00 LT) at 100 m agl, with \( r^2 \) values of 0.87, 0.78 and 0.60, respectively. This result indicates that ozone concentrations at heights above the nocturnal boundary layer were correlated with the ozone concentration at 100 m agl in the following afternoon.

During the early morning hours, the ozone concentrations increase as the altitudes increase to maximum mixing depth. Therefore, the residual ozone can be downward-mixed to the ground and increase surface ozone concentration. Aneja et al. (2000) developed an empirical relationship between maximum ozone concentration measured at the surface during the day and the previous night's average ozone concentration in the residual layer. This study utilized measured 13 data sets to analyze the previous night's average ozone concentration in the residual layer. Thus, the relationship is determined as

\[
O_3^{12,100} = f(NO^{12,12}, NO_2^{12,12}, VOC^{12,12}, NO_3^{10,12}, SO_2^{12,12}, \ldots)
\]

\[
CO_{s}^{1000}, O_3^{1000,3}, O_3^{1000,6}
\]

where CO, NO, NO\(_2\), SO\(_2\), VOCs, and O\(_3\) is concentration for each variable in ppb. Superscripts “s” and “100” denote that a variable was measured at the surface and 100 m agl, respectively. The second superscript (0, 3, 6, 12) denotes LT (00, 03, 06, 12 LT) for the ozone concentration at 1000 m agl in the early morning. VOC\(_{s}^{12}\) is the sum of the styrene and cyclohexane concentrations at the surface, which are better correlated (\( r^2 \) is 0.34 and 0.49, respectively) than other VOC species with the ozone concentration at 100 m agl (Fig. 11).

**High Ozone Concentrations Accompanied Pollutants**

The vertical profile data shows that the ozone concentration peaked at 100-600 m agl (Fig. 7). Experimental data demonstrate that ozone concentration is correlated with precursors (NO, NO\(_2\), VOCs) and ozone concentrations at 1000 m agl at night. Therefore, the relationship between ozone concentration at noon at 100 m agl (\( O_3^{12,12} \)) and its precursors can be written as

\[
O_3^{12,12} = f(NO^{12,12}, NO_2^{12,12}, VOC^{12,12}, NO_3^{10,12}, SO_2^{12,12}, \ldots)
\]

\[
CO_{s}^{1000}, O_3^{1000,3}, O_3^{1000,6}
\]

\[\text{(1)}\]

Table 3. Empirical regression equations for the ozone downward mixing effect.

<table>
<thead>
<tr>
<th>Study site</th>
<th>Linear Eq. ( C_{\text{6am}} = a + b \overline{C}_{\text{3am}} )</th>
<th>Exponential Eq. ( C_{\text{6am}} = a \exp(b \overline{C}_{\text{3am}}) )</th>
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<tr>
<td>Auburn, NC, USA</td>
<td>( a = 28.13 ), ( b = 0.75 ), ( r^2 = 0.42 )</td>
<td>( a = 27.67 ), ( b = 0.016 ), ( r^2 = 0.41 )</td>
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<tr>
<td>Caotun, Nantou, Taiwan</td>
<td>( a = 29.07 ), ( b = 0.91 ), ( r^2 = 0.49 )</td>
<td>( a = 32.92 ), ( b = 0.017 ), ( r^2 = 0.49 )</td>
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<tr>
<td>Caotun, Nantou, Taiwan</td>
<td>( a = 25.87 ), ( b = 1.26 ), ( r^2 = 0.51 )</td>
<td>( a = 40.37 ), ( b = 0.015 ), ( r^2 = 0.51 )</td>
</tr>
</tbody>
</table>

\( \overline{C}_{\text{3am}} \): maximum surface ozone at daytime

\( \overline{C}_{\text{3am}} \): the early morning average ozone concentration above NBL
Eq. (2a) is in the normal units (ppb), and Eq. (2b) is in standardized form, where superscript * denotes the variable in the standardized form. For example, $\bar{O}_3 = (O_3 - \bar{O}_3)/\sigma(O_3)$, where the overbar "—" denotes the mean of the variable, and $\sigma$ is the standard deviation. The p-value of all variables are < 0.002, meaning that these coefficients are statistically significant. Fig. 12 presents a comparison between observed and predicted $O_3$ during the campaign period, which has an $r^2$ of 0.85 (Eq. 2).

The above statistical analysis (Eq. 2) indicates that $SO_2$ is correlated with $O_3$. Nonetheless, $SO_2$ is not a precursor for ozone production. Notably, $SO_2$ is mainly released into the troposphere from high-stack sources, for example, roughly 92% of $SO_2$ and 57% of $NO_2$ was emitted from point sources in the study region (Table 1). And the emission is always accompanied with $NO_2$. Hence, the high ozone concentration is likely related to high-stack sources. Lin et al. (2007) also observed that during an ozone episode, a very high ozone peak was stored aloft in Southern Taiwan; they suspected the high peak likely resulted from an elevated large point source. Moreover, ozone formation has also been observed in power plant plumes in USA by aircrafts (Ryerson et al., 2001). The vertical profiles show that the maximum ozone concentrations occurred around 15 LT at an altitude of 100 m, the $NO_2$ and $SO_2$ profiles also peaked at the same time during episode days (Aug. 16-18) (Figs. 4 and 7).

Strong correlations exist between the ozone concentration and the $NO_2$ and $SO_2$ concentrations at 100 m agl with an $r^2$ of 0.73 and 0.88, respectively (Fig. 11). However, $NO_2$ is not chosen as a variable in Eq. (2), which is due to the collinearity (Neter et al., 2004) between $SO_2$ and $NO_2$ in regression analysis. Note that $NO_2$ was highly correlated with $SO_2$ with $r^2$ of 0.76, but $SO_2$ has been chosen in Eq. (2). Conversely, the correlation between the ozone concentration and $CO$ concentration has a low $r^2$ value of 0.21. In the study region, 73% of $CO$ was emitted from mobile sources (Table 1). Therefore, we conclude that the high ozone concentrations at 100 m agl at the study site were associated more with stack sources than line sources. Note that stack sources (such as nearby power plants) emit both high volumes of $SO_2$ and $NO_2$ pollutants, whereas line sources only emit high volumes of $NO_2$ and relatively less $SO_2$.

**Backward Trajectory Analysis**

Only line sources and no important point sources exist within a 30-km radius of the study site (Fig. 1). Fig. 13 shows the trajectories, calculated by the GTE model developed by Tsuang.
(2003), to the site during 09-12 LT on episode/non-episode days. On episode days (Fig. 13(a)) wind speeds were markedly slower than those during non-episode days, and local circulations, such as land (E)/sea (W) breeze and valley (N)/mountain (S) wind, accompanying the SE monsoon wind caused the trajectories to spiral toward the study site. The trajectories sweep the source pollution along the coast—from power plants (such as TP) and to inland foothill areas, such as the study site. Many point sources were located along the trajectory routes (Fig. 1). In contrast, during non-episode days (Fig. 13(b)), local circulations were not significant and wind speeds were very fast, hence, few sources were carried in the air parcel. Much less point sources were located along trajectory routes during the non-episodes than the episodes. The episodes of particulate matter were also found occurred under strong land-sea breeze conditions in the Basin (Tsong et al., 2003).

Verification

In the above sections, it is suspected that high-stack point sources have an important role in causing the summer ozone episodes in the Basin. Nonetheless, the inference is not well supported because the data is not enough. Note that we only have 12-day O₃ and SO₂ profile data during the campaign. In order to test the hypothesis, we use 11-y summer (June, July and August) daily data at 3 TW/EPA stations (Dali, Nantou and Jhushan) from 1996 to 2006 for further analysis. The total data number is 2523 station days. According to the Principal component analysis (PCA) with varimax normalization (Table 4), it can be seen that

Fig. 13. Backward trajectories from the study site in Caotun on episodes (17th and 18th Aug., 2002) and non-episode (23rd and 25th Aug., 2002), where TP denotes Taichung power plant, and MP denotes Mailiao power plant. The black line denotes trajectories at 09 LT, red at 10 LT, green at 11 LT, blue at 12 LT, light blue at 13 LT, magenta at 14 LT and yellow at 15 LT.
the daily maximum O₃ concentration and the daily mean O₃ concentration are in the same group (Factor 1) as the daily SO₂ concentration for all the three stations, and their signs of the factor loadings are the same. In contrast, the daily CO concentration is in the same group (Factor 2) as the daily NO₂ concentration. It further confirms that high O₃ concentration is more associated with point sources since 92% again of SO₂ was emitted from point sources in the study region. Moreover, the daily NO concentration is, although, in the same group as the O₃ concentration, but their signs of the factor loadings are opposite. It implies that the immediate-upwind emission of NO reduces O₃ concentrations at the three stations in general, likely due to the titration effect (e.g., Chou et al., 2006). Note that the life time of NO is short, only about an hour (Seinfeld and Pandis, 1998). And there are not many point sources near the three stations. Most of the NO emission near the stations was from mobile sources (Figs. 1 and 2).

CONCLUSIONS

This study investigated the vertical distribution of air pollutants and the state of meteorological variables using two tethered balloon system during the 2002 summer in central Taiwan. The observed profile pattern shows a marked vertical convective mixing under unstable atmospheric boundary layers during daylight hours. The nocturnal inversion and valley-mountain wind circulation during episodes were stronger than those during non-episode days.

The concentration profiles of O₃ demonstrate that O₃ concentrations decreased rapidly toward the ground. The photochemical production and convection were stronger at noon and early afternoon than later in the nightfall. During the episode days, the elevated O₃ concentration was confined within the NBL and, thus, preserved its high concentration at nighttime. The emission inventory, trajectory analysis, statistical analysis and empirical relationships indicate that the ozone formed at the foothill study site on episode days were associated more with stack sources than line sources. This suggestion is supported by 11-y summer data at three stations in the Basin.

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REFERENCES


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