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Ozone weekend effects in the Beijing–Tianjin–Hebei metropolitan area, China

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Abstract

The ozone weekend effect (OWE) was first investigated in the metropolitan area of Beijing–Tianjin–Hebei (BTH), China, using in situ measurements from the Atmospheric Environment Monitoring Network from July 2009 to August 2011. The results indicate

- that there is an obvious weekly periodical variation in the surface ozone concentration based on 24 h averaged value. There is a lower ozone concentration from Wednesday to Friday (weekday) and a higher concentration from Saturday to Monday (weekend) over the entire study area. NO_x also displays weekly cycle, with the maximum level occurring on weekdays and the minimum level on weekends, especially later on Sun day night and early Monday morning. This pattern may be responsible for the higher
- ¹⁰ day hight and early wonday morning. This pattern may be responsible for the higher concentration of ozone on weekends. Additionally, the vertical variations in O_3 and NO_x from the 8 m, 47 m, 120 m and 280 m observation platforms on the 325 m Beijing meteorological tower displayed obvious weekly cycles that corresponded to the surface results.
- A smaller decrease in VOCs (a proxy for CO) and much lower NO_x concentrations on the weekend may lead to higher VOC/NO_x ratio, which can enhance the ozone production efficiency in VOC-regime areas. Additionally, a clear weekly cycle in the fine aerosol concentration was observed, with maximum values occurring on weekdays and minimum values occurring on weekends. Higher concentrations of aerosol on weekdays can reduce the UV radiation flux by absorption or scattering, which leads
- to a decrease in the ozone production efficiency. A significant weekly cycle in UV radiation, in consistent with the aerosol concentration, was discovered at the BJT site, validating the assumption. A comprehensive understanding of the ozone weekend effect in the BTH area can provide deep insights into controlling photochemical pollution.



1 Introduction

Surface ozone (O₃), as a main secondary air pollutant, has caused great concern due to its adverse effects on human health and vegetation (NRC, 1991). O₃ is predominantly produced through the photochemical oxidation of non-methane volatile organic compounds (NMVOC_s) and carbon monoxide (CO) in the presence of nitrogen oxides (Fishman and Crutzen, 1978; Seinfeld and Pandis, 1998). Additionally, stratospheric ozone can also be transported into the troposphere and contribute to the concentration of surface ozone. The ozone weekend effect (OWE) is a phenomenon that was first reported in the 1970s (Cleveland et al., 1974; Lebron, 1975; Levitt and Chock, 1976; Karl, 1978). In this phenomenon, the surface ozone concentration in urban areas tends to be higher on weekends than on weekdays despite the lower concentration of ozone precursors (NO_x and volatile organic compounds, VOC_S). Currently, the mechanisms that drive the OWE are still not well understood. The surface ozone concentration is controlled by a series of complex physical and chemical processes in relation to precursor

- emissions, local meteorological conditions and photochemical reactions, along with the city's economic structure and local pollutant emissions. The California Air Resources Board (2003) have proposed several hypotheses to explain the OWE. An appropriate understanding of the OWE may provide insights into the effectiveness of control strate-gies for ozone pollution, because these plans typically focus on reducing the emis-
- sion of ozone precursors. A robust understanding of the OWE can also validate the performance of models by simulating ozone concentrations under different emission scenarios (Koo et al., 2012). The OWE has been extensively studied in American and European countries using in situ measurements, numerical simulations and satellite retrieval (Cleveland and McRae, 1978; Altshuler et al., 1995; Randall et al., 1998; Beirle
- et al., 2003; Fujita et al., 2003; Atkinson-Palombo et al., 2006; Murphy et al., 2007; Koo et al., 2012). However, the study of the OWE in Asia is limited due to the small number of observation sites compared to America and Europe. Only few investigations have



been conducted in Shanghai (Tang et al., 2008), the Kathmandu valley (Pudasainee et al., 2010), Taiwan and Japan (Tasi, 2005; Sadanaga et al., 2008).

The metropolitan area of BHT is located in the centre of northeast Asia, including two megalopolises (Beijing and Tianjin) and several prosperous cities (Baoding, Tanggu,

- Langfang, etc.). Accompanying the rapid growth in traffic and the economy, the photochemical pollution has caused great concern over the last few decades (Wang et al., 2006, 2011; Chan et al., 2008; Chou et al., 2009; Xu et al., 2011; Lin et al., 2011). For example, the ambient air quality standard for ozone has frequently been exceeded, and the hourly averaged concentration of 286 ppb has been recorded (Wang et al.,
- ¹⁰ 2006). NO₂ increased by 5.7 % during the first half of 2011, compared to the same period in 2010 (MEP, 2011), in many key cities for environmental protection in China. In particular, China's new "Twelfth Five-Year Plan" has set a target for total NO_x emissions reductions of 10 % for 2011–2015 (China State Council, 2011; Wu et al., 2012). Studying the OWE can provide us a deep insight into the influence of a decrease in NO_x on surface ozone over a large scale.
 - We investigated horizontal and vertical weekly variation ozone concentration in the BTH region using real-time, online data from the Atmospheric Environment Monitoring Network. Furthermore, simultaneous measurements of NO, NO_x , CO, PM_{10} (particles with aerodynamic equivalent diameters of less than 10 µm) and $PM_{2.5}$ (particles with aerodynamic equivalent diameters of less than 2.5 µm) were also recorded to study
- 20 aerodynamic equivalent diameters of less than 2.5 μm) were also recorded to study the causes of the OWE, in addition to relevant data for ultraviolet radiation that were collected at the Beijing meteorological tower site (BJT).

2 Methodology

2.1 A description of the Atmospheric Environment Monitoring Network

²⁵ Ten sites from the Atmospheric Environment Monitoring Network were used. The network had an extensive coverage over the BTH area and provided a comprehensive



data set for air pollutants (PM₁₀, PM_{2.5}, O₃, NO, NO₂, NO_x, SO₂ and CO) in real time (Tang et al., 2012; Ji et al., 2012). Urban and suburban areas are significantly influenced by local emissions from motor vehicles, coal-fired power plants, and industrial facilities. Therefore, these observation sites, located in urban and suburban areas in the BTH region, were selected for the study of weekly ozone variation. As depicted in Fig. 2, there were four sites in Beijing: the 325 m meteorological tower (BJT), Long-tanhu (LTH), Shuangqinglu (SQL) and Yangfang (YF). In addition, there were two sites

in Tianjin: the 255 m tower of Tianjin (TJT) and Tanggu (TG). There were also, four urban and suburban sites surrounding Beijing and Tianjing: Baoding (BD), Yanjiao (YJ),
 Langfang (LF) and Qian'an(QA). Table 1 lists general information about the sites. The sites were far away from specific point emission sources and were broadly representative of photochemical pollution.

2.2 Instruments and methods

The selected sites were set up according to the US EPA methodological designations (US EPA, 2007), and the measurement instruments were housed in a laboratory that was equipped with an air conditioner. Ozone was measured with a Model 49i or 49c ozone analyser from Thermo Environmental Instruments (TEI), Inc. The ozone analyser had a detection limit of 1 ppbv and a precision of 1 ppbv. CO concentrations were documented using TEI Model 48i instruments, with a detection limit of

- $_{20}$ 0.04 ppmv and a precision of 0.1 ppmv. $\rm NO_x$ and NO concentrations were measured using the TEI Model 42c and 42 CTL analysers. Both of the $\rm NO_x$ analysers had a precision of 0.4 ppbv, and the detection limits for Models 42c and 42 CTL were 0.4 ppbv and 0.05 ppbv, respectively. Ambient air samples for both the NO-NO_x and O_3 analyser were drawn through a 3 m PFA Teflon tube (outside diameter: 12.7 mm; inside
- diameter: 9.6 mm), and the sampling tube inlets were located 1 m above the laboratory. Multipoint calibrations of the O_3 analyser were conducted using a zero air supplier (Model 111) and a calibrator (TE 49c PS). The calibration of the NO-NO_x analyser was conducted with a dynamic gas calibrator (Model 146) in conjunction with a zero



- air supplier (Model 111). Additional, detailed calibration work is described in Tang et al. (2012). The concentrations of particles (PM₁₀ and PM_{2.5}) were measured using a TEOM RP1400 (Thermo Scientific: http://www.thermoscientific.com) with 0.1 µgm⁻³ resolution, $\pm 1.5 \,\mu g \,m^{-3}$ 1 h average precision, $\pm 0.5 \,\mu g \,m^{-3}$ 24 h average precision, and a detection limit of $0.06 \,\mu g m^{-3}$ (1 h average). The filters were exchanged when the 5 loading rates were approximately 40%, and the flow rates were monitored and calibrated monthly. High resolution (5 min averages) data sets of O₃, NO, NO_x, CO, PM₁₀ and PM_{2.5} from July 2009 to August 2011 were obtained, and hourly averaged data were used after applying strict data quality control; no data were available on some davs due to instrument malfunction and power failure. In particular, the data obtained 10 on holidays, such as the Spring Festival, National Day and May Day was removed from our study due to false representation of weekly human activities. Simultaneous measurements of UV radiation were also used to validate the weekly cycle of UV radiation, which is needed for ozone formation. The UV radiation (290-400 nm) was measured
- at the Beijing Tower using CUV3 (Kipp & Zonen, the Netherlands) with an accuracy of 5%. The radiation data were recorded at 1 min intervals, and the daily average values that were used in the study were derived from hourly values that were averaged from minute values. The calibration of the sensor and the quality control for the sample data were described in detail by Hu et al. (2008).
- ²⁰ The Weekend effect has been defined in many ways. We chose to define the weekend effect as the difference (Δ W) in the average ozone concentration of Wednesday, Thursday and Friday minus the average concentration of Saturday, Sunday and Monday. The same definition was also used for the weekly analysis (Forster et al., 2003; Gong et al., 2006; Xia et al., 2007; Ho et al., 2009).



3 Results and discussion

3.1 The weekly cycle of surface ozone concentration

The statistical results for the average O₃, NO and NO_x concentrations and their per cent differences on weekdays and weekends at ten sites are summarised in Table 2. On average, the concentration of the secondary pollutant ozone is significantly low while concentration of the primary pollutant NO_x is high in these urban areas. This effect is attributed to the fact that the urban areas have a NO_x-saturated regime (Wang et al., 2010; Tang et al., 2012). The ozone level ranged from 18.2 ppb (LTH) to 23.9 ppb (YF), whereas NO_x remained a high concentration. The average minimum ozone level

- occurred at LTH, BJT and TG, but the average maximum ozone level occurred at YF, BD and SQL. The surface ozone concentrations were higher on weekends than weekdays, as illustrated in Fig. 1. The higher ozone concentrations of LF, LTH, YF, BD, TG and BJT all occurred on Monday, while the other four sites had higher concentrations on Sunday. The lower ozone concentrations at LF, LTH, BD, TG, SQL, BJT, TJT
- and YJ all occurred on Friday, while they occurred on Wednesday at YF and Saturday at QA. The Monday ozone effect in the BTH area is different than that studies from Phoenix (Atkinson et al., 2006), California (Fujita et al., 2003), Sacramento (Murphy et al., 2007), Mexico City (Stephens et al., 2008), France (Pont et al., 2001), Japan (Sadanaga et al., 2008), Nepal (Pudasainee et al., 2010) and Shanghai (Tang et al., 2000), Interviewed and the statement of the
- 2009), which all had maximum ozone levels on Sunday. The detailed interpretations will be discussed in the next section. We also discovered that sites such as TJT, SQL, BD, and BJT had a slight weekly variation based on ozone anomalies, and these anomalies were usually less than 1 ppbv. Furthermore, we also investigated the OWE, as detailed in Table 2. The OWE was calculated using the following equation:
- ²⁵ Ozone weekend effect (OWE) = ([Weekend] [weekday])/[weekday]

The results in Table 2 indicate that OWE varies from 1.8 % at TJT to 11 % at TG, which suggests that a significant weekly human activity may influence weekly variation in



ozone concentrations at this highly factory located area of TG. However, inner land sites, such as LF, LTH, YF, BD, SQL and BJT, are always subject to large amount of ozone precursor emissions from their daily life, such as vehicle emissions and cooking emissions, which may not vary as significantly as factory emissions on every day of week. Consequently, these sites have a moderate weekend effect compared with TG.

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The vertical ozone concentrations derived from the 8 m, 47 m, 120 m and 280 m platforms of 325 m Beijing meteorological tower are depicted in Fig. 3. There were higher ozone concentrations on the first days of week and lower concentrations on the latter days of week. The maximum ozone value occurred on Monday, while the minimum value occurred on Friday at all observation platforms, corresponding with the surface results. However, the ozone concentration at the high platform had minimal variability, but at the low platform ozone was significantly variable. The OWEs at 8 m, 47 m, 120 m and 280 m are 8.1 %, 7.1 %, 2.7 % and 1.6 %, respectively.

The surface ozone concentration observed at a monitoring site is an integrated quantity that is determined by the timing and strength of upwind precursor emissions and the rates of photochemistry and transport. Ozone formation is initiated by OH radicals, whose concentration profile roughly follows solar radiation and attains maximum level near midday. To extend our understanding of the OWE at an individual site, we describe the daily behavior of surface ozone concentrations, as illustrated in Fig. 4a–j. Typical

- ²⁰ patterns of variation for middle latitude urban cities were observed, and the maximum concentrations were observed at approximately 15:00 LT (Local Time). The surface ozone attained its minimum concentration early in the morning (02:00–06:00 LT), as illustrated in Fig. 4 (a–j), mainly due to a closure of photochemical reactions and NO titration (Seinfeld and Pandis, 1998). The peak values at the ten sites occurred on Sun-
- ²⁵ day or Monday. Sites such as LF (Fig. 4a), LTH (Fig. 4b), YF (Fig. 4c), SQL (Fig. 4f), TJT (Fig. 4h) and YJ (Fig. 4j) had higher concentrations on weekends than early on weekday mornings, especially on Monday and Tuesday, which may be related to a decrease in vehicle emissions on weekend nights. Moreover, we also find an interesting phenomenon in which ozone increases somewhat from 20:00–22:00 LT, particularly



on Monday (at YJ, on Sunday). A slight decrease in vehicle activity during this heavy emission period may be responsible for the episode, according to a report by Wei et al. (2004).

3.2 Causes of the surface ozone weekend effect in the BTH area

$_{\rm 5}$ 3.2.1 Decrease in NOx and CO on the weekend

The BTH area has a high level of NO_x pollution, as documented in Table 2 regardless of the day of the week. With vehicle sales increasing 32%, to 18.1 million, in 2010 compared of 2009 (CATARC and CAAM, 2011), on-road vehicle emission is the main source of NO_v in China (Baker et al., 2008; Wu et al., 2012). The maximum NO_v level occur at BD, TG and SQL, with average concentrations of 70.2 ppb, 61.4 ppb and 10 62.8 ppb on weekdays and 65.8 ppb, 54.6 ppb and 53.9 ppb on weekends, respectively. Contrasting with the high NO_v pollution in surrounding areas, Beijing appears to have progressed in controlling NO_x emissions after the air quality improvements that were made for the 29th Olympic Games (Wang et al., 2010). NO also exhibits high levels in this area, except at YF, YJ and QA. Figure 5a-j illustrates the diurnal variation in the 15 NO concentration at ten sites. A typical diurnal cycle in NO_x, which is dependent on rush hours and photochemical reactions, was also observed, as displayed in Fig. 6a-j. The maximum values occur during the morning rush hours, at approximately 08:00 LT (Fig. 6), followed by a decrease in the late morning due to lower emissions and the rapid growth of the planetary boundary layer (PBL) (Seinfeld and Pandis, 1998). A sec-20 ondary maximum occurs due to the evening rush hours and continues. There is no

- significant decrease in NO and NO_x at night due to the accumulation of pollutants, except at the YF site (Figs. 5c and 6c), which is located on a campus where direct vehicle pollution has limited effect.
- ²⁵ The weekly cycle of NO₂ was investigated by Beirle et al. (2003) using GOME measurements, and they reported a difference between weekdays and weekends that depended on the anthropogenic sources of emissions in Asia. The daily behavior of NO



and NO_x also had pronounced differences, as depicted in Figs. 5 and 6. Monday, Sunday and Saturday had lower levels of NO and NO_x than the other days of the week. In particular, a lower concentration of both NO and NO_x were observed on later night of Sunday and early morning of Monday, and it is mainly due to decreased human activ-

- ⁵ ity. It is widely accepted that the OWE in urban areas is partly attributed to a decrease in titration (NO + O₃ → NO₂ +O₂) (Fishman et al., 1978; Altshuler et al., 1995; Fujita et al., 2003; Murphy et al., 2007; Stephens et al., 2008; Tang et al., 2009), which can lead to an accumulation of ozone late of Sunday night and early Monday morning. The NO titration hypothesis for the BTH area can be validated using daily ozone profiles,
- as illustrated in Fig. 4. Ozone displayed high concentrations on daytime and low concentration on nighttime, which suggest a strong photochemical reaction on this region (Wang et al., 2006). The ozone concentrations were higher on weekend nighttime and lower on weekday nighttime due to the different NO concentration.

The vertical weekly distributions of NO_x concentrations at 8 m, 47 m, 120 m and 280 m are also displayed in Fig. 7. NO_x had high concentration later in the week but a low concentration early in the week at each of the four heights. The minimum concentration all occurred on Monday due to the reduced human emissions and lower accumulation on weekends. The NO_x displayed significant weekend effect on low platform, consisting with OWE at low platform. However, this weekend effect is not significant on high platforms, as depicted in Figs. 3 and 7. Both observation study by Chen et al. (2013) and numerical simulation study by Tang et al. (2010) showed that the peak ozone concentration occurred at nearly 1 km over BTH area, which suggested that surface ozone mainly came from transition of upper atmosphere. The NO_x mainly came from surface emissions, so weekly variation of ozone on low platform was influenced

²⁵ more than high platform by NO_x .

There should be a difference between weekday and weekend VOCs, and the change of VOC/NO_x mixing ratios should also change according to the variation in their sources in this fast developing area, as in other regions of the world (Atkinson-Palombo et al., 2006; Sadanaga et al., 2008; Shao et al., 2009; Pudasainee et al., 2010). However, di-



rect VOC measurements were not used in our analysis. These types of measurements are relatively sparse for the BTH area and have a low temporal resolution (i.e., one sample a week). Here, we use CO as a proxy for VOCs because of their similar origins (Baker et al., 2008), similar to the method that was used by Stephens et al. (2008) for studying the OWE in Mexico City. VOCs are usually several times more reactive

than CO; therefore, it is debatable whether variations in CO can be used as a proxy for variations in VOC reactivity.

Table 3 lists the weekday and weekend differences in CO concentrations at the BJT and TJT sites, but CO data for the other sites are not available. Both CO concentrations at the two sites decrease over the weekend, with a 4.4% decrease at BJT and a 3.2% decrease at TJT. Detailed daily behaviors are illustrated in Fig. 8. The maximum concentration occurred on Wednesday, and the minimum concentration occurred on Monday. Thus, the decrease in VOC concentrations is lesson than the decrease in NO_x (Table 2) on the weekend. Moreover, studies (Wang et al., 2006; Tang et al., 2012) have reported that the BTH area may be under a VOC-limited regime. Consequently, an increased VOC/NO_x ratio on weekends may enhance the ozone production

efficiency and lead to higher ozone concentrations.

3.2.2 Decrease in particles and increase in UV radiation on the weekend

 $\rm PM_{10}$ and $\rm PM_{2.5}$ concentrations from the monitoring sites have also been reported for weekdays and weekends to validate a weekly cycle, along with UV radiation. Our $\rm PM_{10}$ data were collected by TEOM at LF, YF, BD, TG, BJT, YJ and QA, while $\rm PM_{2.5}$ data were collected from LTH, SQL, BJT and TJT.

It is well known that TEOM instruments measure lower particle mass values than the collocated filter based samplers (Cyrys et al., 2001; Xin et al., 2012). The partic-²⁵ ulate material in the inlet was heated to 50 °C to minimise any interference due to the evaporation and condensation of water vapour onto the filter and to obtain a stable and reproducible measurement. However, some semi-volatile aerosol and particle-bound water may leak out due to the heating. In particular, Charron et al. (2004) reported



that the difference between TEOM and gravimetric measurements varies according to temperature and relative humidity. The measured TEOM aerosol concentration maybe misleads our understanding of aerosol pollution to some extent. However, in this case, we focus on the concentration anomaly between weekdays and weekends, which limits the error due to temperature and relative humidity.

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Table 4 lists the aerosol concentrations and percentage differences at the observation sites on weekdays and weekends. The PM₁₀ pollution is serious, with a range of 186.7 μgm⁻³ at the BD site to 105.1 μgm⁻³ at the YJ site on weekdays and 182.2 μgm⁻³ to 98.4 μgm⁻³ on weekends, respectively. The PM_{2.5} also has a high concentration, from 89.1 μgm⁻³ at the SQL site to 61.4 μgm⁻³ at the LTH site on weekdays and 82.2 μgm⁻³ to 58.7 μgm⁻³ on weekends, respectively. In addition, the statistics for the percentage differences, listed in Table 4, indicate that the maximum PM_{2.5} concentration decrease of 10.7 % occurs at BJT, on weekends compared to weekdays. The emissions of PM_{2.5} is more relevant to human activity than PM₁₀ (Xin et al., 2012), and PM_{2.5} decreased more over the weekend than PM₁₀, as indicated in Table 4. Figure 9a–

- PM_{2.5} decreased more over the weekend than PM₁₀, as indicated in Table 4. Figure 9a– j illustrates the daily behaviors of aerosol concentrations at each site. The maximum concentrations usually occur on Friday (Fig. 9a, c–f, g', h, i) or Wednesday (Fig. 9b, g, j), mainly due to the accumulation of pollutants from the beginning of the week. The minimum concentration is observed on weekends, mostly due to a decrease in emissions from vehicles and factories (Gong et al., 2007). The higher particle concentration on wookdays in China was also reported by Gong et al. (2007) using a daily API (air
- on weekdays in China was also reported by Gong et al. (2007) using a daily API (air pollution index).

Aerosols can effect radiation through both absorption and scattering. The absorption of UV radiation by aerosols leads to a reduced availability of photons; however, scat-

tering aerosols may decrease the photon flux received near the surface (Murphy et al., 2007). Some analyses have been conducted and suggested a difference in the UV radiation level on weekends and weekdays due to a difference in the aerosol concentration (Murphy et al., 2007; Tang et al., 2009), but they do not show a direct reduction in UV radiation that photochemical reaction needs. To further investigate the weekly cycle



of aerosol concentrations and its effect on the energy of photochemical reactions, we analysed the weekly variation in UV radiation at the BJT site because data at the other sites were unavailable. Figure 10 illustrates the weekly variation in UV radiation (290–400 nm) at the BJT site. The minimum value was observed on Wednesday, and the maximum value was observed on Sunday, which is generally consistent with the variation in aerosol concentrations at the BJT site. The statistics from Table 5 indicated that UV radiation was 12.16 W m⁻² on weekdays and 12.18 W m⁻² on weekends, based on surface observation, with a difference of 5.4 %.

4 Summary and conclusion

- The ozone weekend effect (OWE) was investigated at 10 surface sites and the meteorological tower over the Beijing–Tianjin–Hebei metropolitan area of China from July 2009 to August 2011. The analysis indicates that all of the sites have higher ozone concentrations on weekends than on weekdays. The urban core sites, such as TJT, SQL, BD and BJT, had slight OWEs, according to ozone anomalies, while other urban sites had larger OWEs. The analysis of NO also revealed a weekly cycle, with the
- maximum level occurring on weekdays and the minimum level occurring on weekends, which implied that a decrease in NO titration on the weekends, especially later Sunday night and early Monday morning, may be responsible for the higher concentration of ozone then. The vertical variations of ozone and NO_x on four platforms of 325 m Beijing
- ²⁰ meteorological tower also displayed significant weekly cycles, consisting with surface results. Moreover, a smaller decrease in VOCs (a proxy of CO) and a much lower concentration of NO_x on weekends may lead to increasing VOC/NOx ratios, which can enhance the ozone production efficiency in VOC-regime areas. This process may be a cause of the OWE in BTH.
- Additionally, a clear weekly cycle in aerosol concentrations was observed at selected sites, with maximum values occurring on weekdays and minimum values occurring on weekends. UV radiation from surface measurements at the BJT site indicated a signif-



icant weekly cycle, consistent with the aerosol concentration. The fact suggested that a higher concentration of aerosol on weekdays may reduce the UV radiation flux by absorption or scattering than that on weekends, and lead to a decrease in photochemical reactions of ozone formation. These results provide additional scientific basis for determining the characteristics of this photochemical pollution, and we hope they will benefit air pollution control efforts in the region.

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References

5

- Altshuler, S. L., Arcado, T. D., and Lawson, D. R.: Weekday versus weekend ambient ozone concentrations: discussion and hypotheses with focus on Northern California, J. Air Waste Manage., 45, 967–972, 1995.
- 5 Atkinson-Palombo, C. M., Miller, J. A., and Balling, R. C.: Quantifying the ozone "weekend effect" at various locations in Phoenix, Arizona, Atmos. Environ., 40, 7644–7658, 2006.
 - Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J., Blake, D. R., and Rowland, F. S.: Measurements of nonmethane hydrocarbons in 28 United States cities, Atmos. Environ., 42, 170–182, 2008.
- Beirle, S., Platt, U., Wenig, M., and Wagner, T.: Weekly cycle of NO₂ by GOME measurements: a signature of anthropogenic sources, Atmos. Chem. Phys., 3, 2225–2232, doi:10.5194/acp-3-2225-2003, 2003.

California Air Resources Board: The Ozone Weekend Effect in California, CARB Planning and Technical Support Division, Sacramento, 2003.

25 CATARC (China Automotive Technology and Research Center) and CAAM (Chinese Association of Automotive Manufactures): China Automotive Industry Yearbooks (in Chinese), China Automotive Technology and Research Center, 2011.

Chan, K. C. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42, 7053–7063, 2008.



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Charron, A., Harrison, R. M., Moorcroft, S., and Booker, J.: Quantitative interpretation of divergence between PM₁₀ and PM_{2.5} mass measurement by TEOM and gravimetric (Partisol) instruments, Atmos. Environ., 38, 415–423, 2004.

Chen, P., Quan, J., Zhang, Q., Tie, X., Gao, Y., and Huang, M.: Measurements of vertical and

- horizontal distributions of ozone over Beijing from 2007–2010, Atmos. Environ., 74, 37–44, doi:10.1016/j.atmosenv.2013.03.026, 2013.
 - China State Council: Comprehensive Framework on Energy Saving and Emission Reduction for the 12th Five Year Plan, http://www.gov.cn/zwgk/2011-09/07/content_1941731.htm (last access: 7 September 2011), (in Chinese), 2011.
- ¹⁰ Chou, C. C. K., Tsai, C. Y., Shiu, C. J., Liu, S. C., and Zhu, T.: Measurement of NO_y during Campaign of Air Quality Research in Beijing 2006 (CAREBeijing-2006): implications for the ozone production efficiency of NO_x, J. Geophy. Res., 114, D00G01, doi:10.1029/2008JD010446, 2009.

Cleveland, W. S., Graedel, T. E., Kleiner, B., and Warner, J. L.: Sunday and workday variations

- in photochemical air pollutants in New Jersey and New York, Science, 186, 1037–1038, 1974.
 - Cleveland, W. S. and McRae, J. E.: Weekend–weekend ozone concentrations in the Northeast United States, Environ. Sci. Technol., 12, 558–563, 1978.

Cyrys, J., Dietrch, G., Kreyling, W., Tuch, T., and Heinrich, J.: PM_{2.5} measurements in ambi-

- ent aerosol: comparison between Harvard impactor (HI) and the tapered element oscillation microbalance (TEOM) system, Sci. Total. Environ., 278, 191–197, 2001.
 - Fishman, J. and Crutzen, P. J.: The origin of ozone in troposphere, Nature, 274, 855–858, 1978.

Forster, P. M. F. and Solomon, S.: Observations of a "weekend effect" in diurnal temperature range, PNAS, 100, 11225–11230, 2003.

Fujita, E. M., Stockwell, W. R., Campbell, D. E., Keislar, R. E., and Lawson, D. R.: Evolution of the magnitude and spatial extent of the weekend ozone effect in California's South Coast Air Basin, 1981–2000, J. Air Waste Manage., 53, 802–815, 2003.

25

Gong, D. Y., Guo, D., and Ho, C. H.: Weekend effect in diurnal temperature range in China: opposite signals between winter and summer, J.Geophys. Res., 111, D18113, doi:10.1029/2006JD007068, 2006.



- Gong, D. Y., Ho, C. H., Chen, D., Qian, Y., Choi, Y. S., and Kim, J.: Weekly cycle of aerosol-meteorology interaction over China, J. Geophys. Res., 112, D22202, doi:10.1029/2007JD008888, 2007.
- Ji, D. S., Wang, Y. S., Wang, L. L., Chen, L. F., Hu, B., Tang, G. Q., Xin, J. Y., Song, T., Wen, T. X.,
- ⁵ Sun, Y., Pan, Y. P., and Liu, Z, R.: Analysis of heavy pollution episodes in selected cities of Northern China, Atmos. Environ., 50, 338–348, 2012.
 - Ho, C. H., Choi, Y. S., and Hur, S. K.: Long-term changes in summer weekend effect over northeastern China and the connection with regional warming, Geophys. Res. Lett., 36, L15706, doi:10.1029/2009GL039509, 2009.
- Hu, B., Wang, Y. S., and Liu, G. R.: Influences of the clearness index on UV solar radiation for two locations in the Tibetan Plateau-Lhasa and Haibei, Adv. Atmos. Sci., 25, 885–896, 2008.

Karl, T. R.: Day of week variations of photo-chemical pollutants in St. Louis area, Atmos. Environ., 8, 1657–1667, 1978.

Koo, B., Jung, J., Pollack, A. K., Lindhjem, C., Jimenz, M., and Yarwood, G.: Impact of meteorology and anthropogenic emissions on the local and regional ozone weekend effect in Midwestern US, Atmos. Environ., 57, 13–21, 2012.

Lebron, F.: A comparison of weekend–weekday ozone and hydro-carbon concentration in the Baltimore–Washington metropolitan area, Atmos. Environ., 9, 861–863, 1975.

- ²⁰ Levitt, S. B. and Chock., D. P.: Weekday-weekend pollutant studies of Los Angeles Basin, Japca. J. Air Waste Ma., 11, 1091–1092, 1976.
 - Lin, W., Xu, X., Ge, B., and Liu, X.: Gaseous pollutants in Beijing urban area during the heating period 2007–2008: variability, sources, meteorological, and chemical impacts, Atmos. Chem. Phys., 11, 8157–8170, doi:10.5194/acp-11-8157-2011, 2011.
- MEP (Ministry of Environmental Protection, P.R. China): Air quality bulletin for key environmental protection cities in the 1st half of 2011, http://www.mep.gov.cn/gkml/hbb/bgg/201107/ W020110730434018324100.pdf ((last access: 30 July 2011), (in Chinese), 2011.
 - Murphy, J. G., Day, D. A., Cleary, P. A., Wooldridge, P. J., Millet, D. B., Goldstein, A. H., and Cohen, R. C.: The weekend effect within and downwind of Sacramento Part 1: Obser-
- vations of ozone, nitrogen oxides, and VOC reactivity, Atmos. Chem. Phys., 7, 5327–5339, doi:10.5194/acp-7-5327-2007, 2007.
 - NRC (National Research Council): Rethinking the Ozone Problem in Urban and Regional Air Pollution, National Academic Press, Washington, DC, USA, 1991.



- Pont, V. and Fontan, J.: Comparison between weekend and weekday ozone concentration in large cities in France, Atmos. Environ., 35, 1527–1535, 2001.
- Pudasainee, D., Sapkota, B., Bhatnagar, A., Kim, S. H., and Seo, Y. C.: Influence of weekdays, weekends and bandhas on surface ozone in Kathmandu valley, Atmos. Res., 95, 150–156, 2010.

5

10

15

30

- Randall, S. C. and Robert, C. B.: Weekly cycles of air pollutants, precipitation and tropical cyclones in the coastal NW Atlantic region, Nature, 394, 561–563, 1998.
- Sadanaga, Y., Shibata, S., Hamana, H., Takenaka, N., and Bandow, H.: Weekday/weekend difference of ozone and its precursors in urban areas of Japan, focusing on nitrogen oxides and hydrocarbons, Atmos. Environ., 42, 4708–4723, 2008.
- Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., and Chen, Z.: Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, J. Geophys. Res., 114, D00G06, doi:10.1029/2008JD010863, 2009.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, from Air Pollution to Climate Changes, Wiley, New York, USA, 1998.

Stephens, S., Madronich, S., Wu, F., Olson, J. B., Ramos, R., Retama, A., and Muñoz, R.: Weekly patterns of México City's surface concentrations of CO, NO_x, PM₁₀ and O₃ during 1986–2007, Atmos. Chem. Phys., 8, 5313–5325, doi:10.5194/acp-8-5313-2008, 2008.

Tang, G.: Modeling of ozone spatial-temporal distribution in the vicinity of Beijing during

- ²⁰ Olympics, PhD thesis, Chinese Academy of Sciences, Institute of Atmospheric Physics, 2010.
 - Tang, G., Li, X., Wang, Y., Xin, J., and Ren, X.: Surface ozone trend details and interpretations in Beijing, 2001–2006, Atmos. Chem. Phys., 9, 8813–8823, doi:10.5194/acp-9-8813-2009, 2009.
- Tang, G., Wang, Y., Li, X., Ji, D., Hsu, S., and Gao, X.: Spatial-temporal variations in surface ozone in Northern China as observed during 2009–2010 and possible implications for future air quality control strategies, Atmos. Chem. Phys., 12, 2757–2776, doi:10.5194/acp-12-2757-2012, 2012.

Tang, W. Y., Zhao, C. S., Geng, F. H., Peng, L., Zhou, G. Q., Xu, J. M., and Tie, X. X.: Study of ozone "weekend effect" in Shanghai, Sci. China Ser. D, 51, 1354–1360, 2008.

Tasi, Y. I.: Atmospheric visibility trends in an urban area in Taiwan 1961–2003, Atmos. Environ., 39, 5555–5567, 2005.



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Discussion Paper

Discussion Paper

Discussion Paper

US EPA, Environmental Protection Agency 40 CFR Parts 53 and 58 [EPA-HQ-OAR-2004-0018: FRL-] RIN 2060-AJ25, http://www.epa.gov/ttn/amtic/files/ambient/pm25/092706sign. pdf (last access: 15 May 2013), 2004.

Wang, T., Ding, A., Gao, J., and Wu, W. S.: Strong ozone production in urban plumes from Beijing, China, Geophys. Res. Lett., 33, L21806, doi:10.21029/22006GL027689, 2006.

- Beijing, China, Geophys. Res. Lett., 33, L21806, doi:10.21029/22006GL027689, 2006.
 Wang, T., Nie, W., Gao, J., Xue, L. K., Gao, X. M., Wang, X. F., Qiu, J., Poon, C. N., Meinardi, S., Blake, D., Wang, S. L., Ding, A. J., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, Atmos. Chem. Phys., 10, 7603–7615, doi:10.5194/acp-10-7603-2010, 2010.
- Wang, Y., Zhang, Y., Hao, J., and Luo, M.: Seasonal and spatial variability of surface ozone over China: contributions from background and domestic pollution, Atmos. Chem. Phys., 11, 3511–3525, doi:10.5194/acp-11-3511-2011, 2011.

Wei, M., Chen, L., Chi, R., Cao, Z., and Yang, F.: Survey and analysis of traffic flow at typical intersection of congested road in Beijng, Journal of China Agricultural University, 9, 91–95, (in Chinese), 2004.

Wu, Y., Zhang, S. J., Li, M. L., Ge, Y. S., Shu, J. W., Zhou, Y., Xu, Y. Y., Hu, J. N., Liu, H., Fu, L. X., He, K. B., and Hao, J. M.: The challenge to NO_x emission control for heavy-duty diesel vehicles in China, Atmos. Chem. Phys., 12, 9365–9379, doi:10.5194/acp-12-9365-2012, 2012.

15

- Xia, X., Eck, T., Holben, B., Phillippe, G., and Chen, H.: Analysis of the weekly cycle of aerosol depth using AERONET and MODIS data, J. Geophys. Res. Atmos., 113, D14217, doi:10.1029/2007JD009604, 2008.
 - Xin, J., Wang, Y., Tang, G., Wang, L., Sun, Y., Wang, Y. H., Hu, B., Song, T., Ji, D. S., Wang, W. F., Li, L., and Liu, G. R.: Variability and reduction of atmospheric pollutants in
- Beijing and its surrounding area during the Beijing 2008 Olympic Games, Chinese Sci. Bull.,
 55, 1937–1944, doi:10.1007/s11434-010-3216-2, 2010.
 - Xin, J., Wang, Y., Wang, L., Tang, G., Sun, Y., Pan, Y., Ji, D.: Reduction of PM_{2.5} in Beijing– Tianjin–Hebei urban Agglomerations during the 2008 Olympic Games, Adv. Atmos. Sci., 29, 1330–1342, 2012.
- Xu, J., Ma, J. Z., Zhang, X. L., Xu, X. B., Xu, X. F., Lin, W. L., Wang, Y., Meng, W., and Ma, Z. Q.: Measurements of ozone and its precursors in Beijing during summertime: impact of urban plumes on ozone pollution in downwind rural areas, Atmos. Chem. Phys., 11, 12241–12252, doi:10.5194/acp-11-12241-2011, 2011.



Xu, W. Y., Zhao, C. S., Ran, L., Deng, Z. Z., Liu, P. F., Ma, N., Lin, W. L., Xu, X. B., Yan, P., He, X.,
 Yu, J., Liang, W. D., and Chen, L. L.: Characteristics of pollutants and their correlation to meteorological conditions at a suburban site in the North China Plain, Atmos. Chem. Phys., 11, 4353–4369, doi:10.5194/acp-11-4353-2011, 2011.



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Table 1. General information about the sites and parameters used in the study.

Site	Site type	Longitude	Latitude	Altitude	Parameter
Langfang (LF)	Suburban	116.69	39.55	19	O_3 , NO, NO _x and PM ₁₀
Longtanhu (LTH)	Urban	116.43	39.87	40	O_3 , NO, NO _x and PM _{2.5}
Yangfang (YF)	Suburban	116.13	40.15	40	O_3 , NO, NO _x and PM ₁₀
Baoding (BD)	Urban	115.44	38.82	4	O_3 , NO, NO _x and PM ₁₀
Tanggu (TG)	Urban	117.72	39.04	13	O_3 , NO, NO _x and PM _{2.5}
Shuangqinglu (SQL)	Urban	116.34	40.01	58	O_3 , NO, NO _x and PM _{2.5}
Beijing Tower (BJT)	Urban	116.37	39.97	44	O_3 , NO, NO _x , CO, PM _{2.5} , PM ₁₀ and UV
Tianjin Tower (TJT)	Urban	117.21	39.08	2	O_3 , NO, NO _x , CO, PM ₁₀ and PM _{2.5}
Yangjiao (YJ)	Suburban	116.82	39.96	26	O_3 , NO, NO _x and PM ₁₀
Qian'an (QA)	Urban	118.80	40.10	38	O_3 , NO, NO _x and PM ₁₀

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Table 2. Weekday and weekend differences in O_3 , NO and NO_x at these sites.

	Wee	kday (p	pbv)	Wee	kend (p	pbv)	Δ	W (pp	bv)	Per	centage	e (%)
	O ₃	NO	NO_x	O ₃	NO	NO_x	O ₃	NO	NO_x	O ₃	NO	NO_x
LF	21.9	23.1	51.4	23.7	20.8	47.6	1.8	2.3	3.8	8.2	10	7.3
LTH	17.6	26.3	55.2	18.7	25.6	53.1	1.1	0.7	2.1	6.2	2.6	3.8
YF	23.3	6.4	23.2	24.4	5.3	20.7	1.1	1.1	2.5	4.7	17	10.8
BD	23.4	34.3	70.2	24.0	31.6	65.8	0.6	2.7	4.4	2.6	7.9	6.3
ΤG	17.2	29.8	61.4	19.1	25.3	54.6	1.9	4.5	6.8	11	15.1	11.1
SQL	22.2	36.7	62.8	23.4	29.5	53.9	1.2	7.2	8.9	5.5	19.6	14.2
BJT	17.3	24.0	54.5	18.7	22.2	49.8	1.4	1.8	5.7	8.1	7.5	10.5
TJT	22.4	24.7	51.8	22.8	22.3	46.7	0.4	2.4	5.1	1.8	9.7	9.8
YJ	21.1	12.8	32.9	22.5	11.2	29.4	1.4	1.6	3.5	6.6	12.5	10.6
QA	18.6	14.9	36.7	19.7	13.5	34.1	1.1	1.4	2.6	5.9	9.4	7.1



Table 3. Weekday and weekend differences in CO concentrations at the BJT and TJT sites.

	Weekday	Weekend	ΔW	Percentage
	(ppbv)	(ppbv)	(ppbv)	(%)
BJT	1656.5	1582.1	74.4	4.4
TJT	1337.4	1294.3	43.1	3.2

Table 4. Weekday and weekend differences of aerosol concentrations at these sites.

	Weekday	Weekend	ΔW	Percentage
	(µg m ⁻³)	(µg m ⁻³)	(µg m ⁻³)	(%)
LF(PM ₁₀)	161.6	153.7	7.9	4.9
$LTH(PM_{2.5})$	61.4	58.7	2.7	4.4
$YF(PM_{10})$	105.7	99.6	6.1	5.8
BD(PM ₁₀)	186.7	182.2	4.5	2.4
TG(PM ₁₀)	136.5	130.1	6.4	4.7
SQL(PM _{2.5})	89.1	82.2	6.9	7.7
BJT(PM _{2.5})	68.9	61.5	7.4	10.7
BJT(PM ₁₀)	140.7	132.9	7.8	5.5
TJT(PM _{2.5})	68.2	63.5	4.7	6.9
YJ(PM ₁₀)	105.1	98.4	6.7	6.4
QA(PM ₁₀)	158.6	150.9	7.7	4.9

Table 5. Weekday and weekend difference in UV radiation at the BJT site.

Weekday	Weekend	ΔW	Percentage
(Wm ⁻²)	(Wm ⁻²)	(Wm ⁻²)	(%)
12.16	12.18	0.66	5.4

Fig. 1. Weekly variation of surface ozone concentration anomalies at these sites.

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Fig. 3. Weekly variation in ozone concentrations on 8 m, 47 m, 120 m and 280 m platforms of the Beijing meteorological tower.

Fig. 7. Weekly variation in NO_x concentration on 8 m, 47 m, 120 m and 280 m observation platforms of the Beijing meteorological tower.

Fig. 8. Weekly variation of CO concentrations at the BJT site and the TJT site.

Fig. 10. Weekly variation in UV (290-400 nm) radiation at the BJT site.

