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Surface gas pollutants in Lhasa, a highland city of Tibet: current levels and pollution implications

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Abstract

Through several years of development, the city of Lhasa has become one of the most populated and urbanized areas on the highest plateau in the world. In the process of urbanization, current and potential air quality issues have been gradually concerned. To investigate the current status of air pollution in Lhasa, various gas pollutants including NO_x, CO, SO_2 and O_3 were continuously measured from June 2012 to May 2013 at an urban site (29.40° N, 91.08° E, 3650 m a.s.l.). The seasonal variations of primary gas pollutants exhibited a peak from November to January with a large variability. High concentrations of primary trace gases almost exclusively occurred under low wind speed and showed no distinct dependence on wind direction, implying local urban emissions to be predominant. A comparison of NO_2, CO and SO_2 concentrations in summer between 1998 and 2012 indicated a significant increase in emissions of these gas pollutants and a change in their intercorrelations, as a result of a substantial growth in the demand of energy consumption using fossil fuels instead of previously widely used biofuels. The pronounced diurnal double peaks of primary trace gases in all seasons suggested automobile exhaust to be a major emission source in Lhasa. The secondary gas pollutant O_3 displayed an average diurnal cycle of a shallow flat peak for about 4–5 h in the afternoon and a minimum in the early morning. Nighttime O_3 was sometimes completely consumed by the high level of NO_x. Seasonally, the variations of O_3 concentrations displayed a low valley in winter and a peak in spring. In autumn and winter, transport largely contributed to the observed O_3 concentrations, given its dependence on wind speed and wind direction, while in spring and summer photochemistry played an important role. A more efficient buildup of O_3 concentrations in the morning and a higher peak in the afternoon was found in summer 2012 than in 1998. An enhancement in O_3 concentrations would be expected in the future and more attention should be given to O_3 photochemistry in response to increasing precursor emissions in this area.

ACPD
14, 11787–11814, 2014

1 Introduction

The Tibetan plateau, with an average altitude of about 4000 m, is the highest plateau in the world. The capital city of Tibet, Lhasa, is one of the most populated and urbanized areas in this region. Lhasa lies on the northern bank of the Lhasa River in the Lhasa River Valley, which runs west to east and is surrounded by mountains. There are currently 200 thousand inhabitants and a floating population of nearly 400 thousand within an urban area of about 63 km^2. The number of automobiles in Lhasa was already over 150 thousand at the end of 2012.

In Lhasa, gas pollutants including nitrogen oxides (NO_x=NO+NO_2), carbon monoxide (CO), sulfur dioxide (SO_2) and volatile organic compounds (VOCs) are mainly from automobile exhaust, heating, kitchen, small light industries and incense burning in temples. At a high altitude above 3650 m, the content of oxygen in Lhasa is about 68 % of that at the sea level. Incomplete fuel combustion in the low oxygen-containing atmosphere undoubtedly enhances atmospheric pollutants of vehicular origin (Chaffin and Ullman, 1994; Bishop et al., 2001; Nagpure et al., 2011). These atmospheric pollutants impair the visibility and degrade the air quality. Moreover, the secondary gas pollutant ozone (O_3) can be generated by its precursors NO_x and VOCs in the presence of sunlight (e.g., Haagen-Smit, 1952; Haagen-Smit et al., 1953; Seinfeld and Pandis, 1998). Surface O_3 pollution is one of the most stubborn and pervasive environmental problems in the world. At a high concentration, O_3 is harmful to human health and the ecosystem (Chameides et al., 1994; Jacobson, 2002). The atmosphere in Lhasa was found to be photochemically active (Lin et al., 2008). A concern should thereby be raised on the O_3 problem, given the increasing emissions of O_3 precursors in the process of urbanization.

Most efforts have previously been exerted on exploring the O_3 valley and O_3 vertical profiles over the Tibetan Plateau by satellite observations (Guo et al., 2012), ozone sondes (Shi et al., 2000; Tobo et al., 2008; Bian et al., 2012) and model simulations (Liu et al., 2003; Tang and Prather, 2012). Investigations on surface trace gases have

ACPD
14, 11787–11814, 2014

rarely been reported for Lhasa, the rapidly growing capital city of Tibet (Yu et al., 2001; Zhou et al., 2001; Tang et al., 2002; Dechen et al., 2008). In comparison with many other cities in China (He et al., 2002 and the references therein), air quality in Lhasa was quite fine. However, with thriving tourism and economy in the process of urbanization, more and more pollutants are expected to be accumulated within the city due to the valley topography. In this paper, analysis of systematically collected data of surface O_3, NO_x, CO and SO_2 during one year is presented and discussed. The observational site and instruments are described in Sect. 2. An overview of meteorology is given in Sect. 3.1. Seasonal and diurnal variations of the gas pollutants are presented in Sect. 3.2, followed by a discussion on how meteorology could influence observed concentrations of gas pollutants in Sect. 3.3. A possible impact of urbanization on air quality in Lhasa in past decades is discussed in Sect. 4. Finally is the summary.

2 Observations

2.1 The site

Lhasa sits in a flat river valley in the Himalaya Mountains (Fig. 1a). Located at the bottom of a small basin surrounded by the Himalaya Mountains, Lhasa has an elevation of about 3650 m and lies in the center of the Tibetan Plateau with the surrounding mountains rising to 5500 m. The Lhasa River (or Kyi Chu), a tributary of the Yarlung Zangbo River, runs through the southern part of the city. The marshlands, mostly uninhabited, are to the north of the city. Ingress and egress roads run east and west.

The observational site (29.40° N, 91.08° E, 3650 m a.s.l.) for this study is at a meteorological and atmospheric composition monitoring station, located in a residential and commercial area in urban Lhasa (Fig. 1b). The site is about 2 km east of the famous Potala Palace. There are also another two famous temples (Jokhang Temple and Ramoche Temple) within the surrounding 1 km^2 of the site. In addition, measurements of trace gases were also conducted in summer 1998 at a suburban site to the

ACPD
14, 11787–11814, 2014

east of the city centre (29.65° N, 91.16° E, 3650 m a.s.l.). This suburban site was located in large areas of farms with sparsely interspersed residency 15 years ago, but now already within the populated areas of Lhasa after its continuous expansion and development.

2.2 Instruments and data

Surface trace gases were continuously monitored for one year from June 2012 to May 2013, using commercial instruments installed on top of a 20 m high building at the site. Observations of CO and SO_2 started from August 2012. Missing CO data from 28 April 2013 to 16 May 2013 was due to a malfunction of the CO analyzer.

A UV photometric analyzer (Model 49C) from Thermo Electron Corporation (TE, USA) was used to determine O_3 concentrations. CO was measured with a gas filter correlation analyzer (TE 48CTL). SO_2 was measured with a pulsed fluorescence analyzer (TE 43CTL). EC9841B/ECOTECH nitrogen oxides analyzer with a heated molybdenum NO_2 to NO converter and the chemiluminescence technique was used to simultaneously quantify concentrations of NO and NO_x. According to USEPA recommendations on quality assurance and quality control (USEPA, 2008), multipoint calibrations were operated every month using a dynamic gas calibrator (Gascal 1100, Ecotech, Australia) and a zero air supplier (Eco Physics PAG003, Switzerland), together with the standard reference gas mixture ($NO/CO/SO_2$ in N_2). The O_3 analyzer was calibrated using the TE 49CPS calibrator. Particularly, zero checks for the CO analyzer were automatically performed every 2 h to record zero drifts, using the SOFNOCAT 514 oxidation catalyst (Molecular Products Asia Ltd, UK) and a 3-way solenoid valve. Ambient concentrations of trace gases were recorded as 1 min averages (mixing ratios by volume, ppbv).

Meteorological data were obtained from an Automatic Weather Station at the site. Wind speed and wind direction were measured at 10 m height, reported as 10 min average wind speed and 10 min smoothing wind direction based on 1 s sampling data for each hour. Other parameters including temperature, relative humidity and precipitation

ACPD
14, 11787–11814, 2014

were observed at 1.5 m height and reported in hourly averages. Cloud amount was recorded four times each day, respectively at 00:00, 06:00, 12:00 and 18:00 LST.

At the suburban site, measurements of O_3, NO_2, CO and SO_2 concentrations were carried out from June to September 1998 on top of a 3-storey building (Tang et al., 2002). O_3 concentrations were measured by a UV photometric analyzer (TE 49C), which was calibrated using the TE 49CPS calibrator. CO gas correlation filter (GFC, Advanced Pollution Instruments Inc, USA) with the non-dispersive infrared (NDIR) technique was used to monitor the low level of CO concentrations. Also due to the extremely low level of NO_2 and SO_2 concentrations in Lhasa at that time, the air was sampled for 4170 min by filter-based samplers every 3 to 4 days. Concentrations of NO_2 and SO_2 were quantified in the laboratory by the DX-500 ion chromatography system (Dionex, USA) and reported in ppbv.

3 Results and discussion

3.1 An overview of meteorology

Situated on the Tibetan Plateau, Lhasa has a very high level of ultraviolet radiation, especially in the summer, due to the high altitude, the low latitude and the tenuous atmosphere (Pu Bu et al., 1997; Ren et al., 1999; Norsang et al., 2009). With strong solar radiation in the daytime, the maximum air temperature could still reach as high as 15.8 °C even in the coldest month January, when the average air temperature was below zero and the minimum was −11.4 °C . The highest monthly average of 18.1 °C and daily maximum of 28.9 °C were found in June. The weather in the rainy season from May to September was generally warm, humid and cloudy. Monthly averages of the temperature and relative humidity ranged from 13.3 ± 5.2 °C to 18.1 ± 4.4 °C and from 41 % to 60 %, respectively. In the rainy season, the precipitation amounted to 368 mm, about 94 % of the total amount in the year (Fig. 2). Despite the large amount of frequently observed precipitation in the rainy season, particularly in summer from June

ACPD
14, 11787–11814, 2014

to August, most of the precipitation occurred at night (18:00–06:00 LST), accounting for 84 % of the total amount during this period. In the rest of the year, it was usually dry and cloud-free. There was hardly any precipitation from October to March. During this period, around 46 % of the days were clear in the daytime based on the cloud amount, while at night the fraction rose to about 74 %. Monthly averages of the temperature and relative humidity ranged respectively from $-0.1 \pm 5.8\,^{\circ}C$ to $10.6 \pm 5.5\,^{\circ}C$ and from 14 % to 27 % in the dry period.

The frequency of wind direction in each season is displayed in Fig. 3 by the wind rose. Wind direction was mainly found in the WSW–WNW and ENE–ESE sector (Fig. 3a), as a result of the orientation of the Lhasa River Valley. The mountains to the north and south of the city significantly inhibited winds in these directions, especially those with a wind speed above $2\,m\,s^{-1}$. The frequency of northerly winds was though comparable with that of easterly or westerly winds, the wind speed of northerly winds was exclusively under $2\,m\,s^{-1}$ (Fig. 3b). The observed 10 min average wind speed was mostly smaller than $2\,m\,s^{-1}$ (close to 65 %), with the annual average occurrence of calm conditions to be about 10 % and the frequency of wind speed larger than $2\,m\,s^{-1}$ around 25 %. High wind speed was usually observed in the afternoon in summer and autumn.

3.2 Seasonal and diurnal variations of gas pollutants

Monthly averages of O_3, O_x ($O_3 + NO_2$), NO, NO_x, CO and SO_2 concentrations were displayed in Fig. 4. Ozone and total oxidant O_x exhibited similar seasonal variations, with the peak in spring and the low valley in winter. The maximum monthly mean concentrations of O_3 and O_x were observed in May, respectively as 56.8 ± 10.1 ppbv and 70.1 ± 10.6 ppbv. The highest monthly O_3 average concentration observed in Lhasa was slightly higher than that of 54.8 ± 18.1 ppbv observed in June 2007 at a rural site Gucheng, which was thought to have good regional representativeness of the North China Plain, one of the most polluted regions in the world (Lin et al., 2009). The highest hourly O_3 concentration of 90.6 ppbv in Lhasa was also observed in May. The low-

ACPD
14, 11787–11814, 2014

est monthly mean concentrations of O_3 and O_x were 22.9 ± 4.0 ppbv in December and 39.5 ± 4.1 ppbv in January.

The air in Lhasa was mostly polluted from November to January with respect to the levels of SO_2 (2.72 ± 2.05 ppbv) and O_3 precursors NO_x (29.58 ± 16.16 ppbv) and CO (570 ± 300 ppbv), possibly as a result of slowed removal processes, increased emissions and accumulation within the boundary layer. In the rest of the year, SO_2, CO and NO_x averaged 0.77 ± 0.61 ppbv, 363 ± 94 ppbv, and 17.10 ± 6.19 ppbv, respectively. The highest daily mean concentrations of SO_2, CO, NO, and NO_x were respectively 14.50 ppbv, 2097 ppbv, 74.12 ppbv, and 97.2 ppbv, occurring on 18 December 2012.

Diurnal variations of O_3, O_x, NO, NO_x, CO and SO_2 concentrations in spring (March–May), summer (June–August), autumn (September–November) and winter (December–February) were plotted in Fig. 5. The diurnal cycle of O_3 concentrations averagely exhibited a shallow flat peak for about 4–5 h in the afternoon and a minimum in the early morning throughout the year. O_3 concentrations reached about 57 ppbv in the afternoon (12:00–17:00 LST) in spring, when meteorological conditions favored O_3 photochemical production. In summer and autumn, O_3 concentrations averaged over the afternoon were close to 48 ppbv, and the lowest average value was observed in winter as 37 ppbv. Nighttime O_3 concentrations were much higher in spring and summer than in autumn and winter, which was mainly attributed to a large amount of NO emissions from heating in the cold weather. As for other gas pollutants, pronounced double peaks in the diurnal variations could be clearly identified in all seasons. The morning peaks (around 07:00 LST) and the evening peaks (around 20:00 LST) resulted from enhanced traffic emissions in the rush hours as well as the diurnal variations of the boundary layer. Concentrations of O_3 precursors and SO_2 were found to be highly variable during the rush hours and the night, especially in autumn and winter. The termination of photochemical reactions and the breakup of the boundary layer should be responsible for a stronger evening peak compared to the morning peak.

ACPD
14, 11787–11814, 2014

3.3 Influences of meteorology on gas pollutants

As for the secondary gas pollutant O_3, meteorology could exert an influence on the ambient concentrations by transport and accelerating or decelerating the photochemical reactions. In spring and summer, the weather was generally warm and sunny in the daytime, favoring O_3 photochemical production. No distinct dependence of O_3 concentrations on wind speed and wind direction was found in spring and summer (figure not shown here), suggesting that O_3 photochemistry might play an important role in the observed concentrations. Occasionally, O_3 pollution events could be observed at night in spring when easterly winds above $2\,m\,s^{-1}$ prevailed for several hours and brought in O_3-rich air. A pollution event is defined here as the hourly average concentration exceeding 80 ppbv for O_3, 50 ppbv for NO_x, 1000 ppbv for CO and 10 ppbv for SO_2, respectively. Table 1 gives the exceedance frequency based on hourly trace gas averages in each season. The occurrence of O_3 pollution events were only found in spring and summer, majorly in the afternoon in spring. In autumn and winter, the transport process instead of the photochemical process probably made a major contribution to the ambient O_3 concentrations. On average, O_3 concentrations were found to be nearly 10 ppbv higher in the SW–NW sector than in other directions. With increasing wind speed, the concentrations of O_3 also slightly increased.

The dependence of primary gas pollutants on wind followed a similar pattern throughout the year (figure not shown here). The ambient concentrations of NO_x, CO and SO_2 were quite high under low wind speed (smaller than $2\,m\,s^{-1}$) and decreased sharply as the wind speed increased. There was a slight dependence of NO_x, CO and SO_2 concentrations on wind direction only under low wind speed, showing a higher level in the NW–N sector, indicating that local emissions of automobiles and heating as well as incense burning to be dominant in Lhasa. High concentrations of primary gas pollutants were mainly observed in autumn and winter (Table 1). Almost 90 % of the pollution episodes occurred at calm night in autumn and winter, when chemical transformation of primary gases were slowed down and the accumulation was favored. The

ACPD
14, 11787–11814, 2014

highest hourly concentrations of SO_2, CO, NO, and NO_x occurred near midnight in December or January, and were 63.44 ppbv, 8511 ppbv, 412.36 ppbv, and 468.43 ppbv, respectively. The hourly maxima of CO concentrations in Lhasa were almost comparable with that at Gucheng and Wuqing, two sites well representative of the regional pollution in the North China Plain (Lin et al., 2009; Xu et al., 2011). The occurrence frequency of hourly CO concentrations above 3000 ppbv, which could approximately be taken as the average level in winter in the North China Plain, ranged from 7 % to 16 %. The hourly maxima of NO and NO_x concentrations were much higher than that of 202 ppbv and 300 ppbv in the megacity of Beijing in the heating season from November 2007 to March 2008, despite that the averages in Lhasa were about 30 ppbv lower during that period (Lin et al., 2011). Hourly NO_x concentrations above the average level of 60 ppbv observed during the heating season in Beijing accounted for around 70 % of the period from October to February in Lhasa. The level of SO_2 concentrations in Lhasa was much lower, compared to a concentration of several ppbv in summer to tens of ppbv in winter in the North China Plain (Lin et al., 2012). The occurrence frequency of hourly SO_2 concentrations above the average level of 30 ppbv in the heating season in Beijing ranged from 3 % to 6 %. Generally, primary gas pollution has been quite noticeable in Lhasa in the cold season.

3.4 Impacts of urbanization on air pollution

Lhasa has undergone remarkable changes in the process of urbanization in the past decades. The area of the city has currently been enlarged almost twice of that as 34 km^2 in 1998, when the measurements of trace gases at the suburban site took place. The permanent and floating population has been explosively expanding, as well as the number of automobiles. According to the municipal statistical data, the permanent population in Lhasa was only 43 thousand in 1998, about one quarter of that now. The number of tourists has dramatically increased from 200 thousand per year in 1998 to 6.5 million in 2012. Compared to over 150 thousand automobiles in 2012, the number was less than 10 thousand in 1998. The gross domestic product of Lhasa amounted to

ACPD
14, 11787–11814, 2014

2.9 billion and 26.2 billion respectively in 1998 and 2012. The fast development during urbanization has led to a substantial growth in the demand of energy consumption. As a result, the urban heat island intensity of Lhasa has increased from 1.8 °C in 1998 to 2.2 °C in 2012 based on the meteorological data. At the same time, the energy structure in Lhasa has been through a significant change. In 1998, biofuels such as cow dung, faggots and leaves were widely used by local residents. Petroleum products and coals only contribute a negligible portion to the fuel mix in this region. Nowadays, however, fossil fuel has become an important component of consumed energy sources. Along with the enhanced energy consumption and the transformation of fuel mix, the level of atmospheric pollutants has risen year by year. Undoubtedly, this would give rise to notable environment problem in Lhasa.

A comparison was made between the levels of NO_2, SO_2, CO and O_3 measured during June and September respectively in 1998 and 2012 (Fig. 6). Generally, it was found that the current average level of NO_2 in summertime was about 15 ppbv, almost 40 times of NO_2 concentrations 15 years ago. During the sampling period in 1998, measured NO_2 concentrations never exceeded 1 ppbv. In contrast, the lowest daily mean concentration of NO_2 was around 9 ppbv and the highest value was close to 27 ppbv in summer 2012, clearly indicating a marked increase in NO_x emissions, which are largely from vehicular exhaust in urban Lhasa. A comparatively smaller change has been observed in SO_2 concentrations, with an increase in the average level of SO_2 from about 0.15 ppbv to 0.5 ppbv. The highest hourly SO_2 average observed in summer 2012 was around 5 ppbv. In Lhasa, SO_2 is mostly from coal burning and less from vehicular exhaust and incense burning. The demand of coals has taken a relatively slower pace than that of petroleum as fuel of automobiles. Incense burning, which gives off SO_2, NO_x and many other pollutants, is a tradition for residents in Lhasa as well as ever increasing tourists who believe in Buddhism. Generally, the process of urbanization and commercialization in Lhasa has resulted in more severe NO_2 pollution than SO_2 pollution according to our measurements.

ACPD
14, 11787–11814, 2014

CO has a much longer lifetime in the atmosphere than NO_2 and SO_2, thereby implying fingerprints of the regional background and the influence of transport more than that of local emissions. On average, there was no apparent diurnal cycle of CO in Lhasa in summer 1998. Nighttime CO concentrations were about 500 ppbv, nearly 1.7 times of that during the daytime. However, distinct double peaks of CO concentrations in the morning and evening were observed in summer 2012 as shown in Fig. 5. The differences in the average diurnal variations of CO concentrations between 1998 and 2012 revealed an average increase in the rush hours reaching up to about 180 ppbv, while a decrease to the same extent at night where a large variability of CO concentrations in summer 2012 was also found (Fig. 7a). During the daytime, CO concentrations in summer 1998 were almost level with that in summer 2012. Such changes in the observed diurnal cycles of CO concentrations probably suggest increased CO emissions from automobiles in the rush hours. Unfortunately, diurnal cycles of NO_x concentrations in 1998 were not available to further confirm above conclusion.

A further examination of the SO_2/CO, NO_x/CO and SO_2/NO_x ratios was performed to cast more light on emission sources of the primary gases. Reduced major axis regression of the hourly average data was employed to account for measurement errors of each trace gas. It was found that the correlation coefficients (R) of SO_2 with CO and SO_2 with NO_x were above 0.9 in a significant level ($P < 0.001$) in autumn and winter 2012, while in spring less than 0.7 and in summer less than 0.4 (Fig. 8a and c). In contrast, NO_x and CO concentrations were well correlated (R was 0.83, 0.77, 0.92, 0.95, respectively in spring, summer, autumn and winter) throughout the year (Fig. 8b). The good correlations among primary gas pollutants in autumn and winter suggested common sources of SO_2, NO_x and CO in cold seasons, when the emission from coal burning for heating was thought to be the major source of primary gas pollutants in Lhasa. The poor correlations of SO_2 with both NO_x and CO in spring and especially in summer, as well as the rather low SO_2 concentrations compared with that in cold seasons, indicated that the major source of SO_2 was different from that of CO and NO_x, which were mainly from gasoline and biofuel burning in warm seasons. Besides,

ACPD
14, 11787–11814, 2014

the far more efficient wet deposition of SO_2 than CO and NO_x in rainy spring and summer could also partially explain lower correlation coefficients of SO_2 with CO and SO_2 with NO_x in spring and summer than in autumn and winter. Figure 8d shows the scatter plots of SO_2 vs. CO and NO_2 vs. CO during June and September in 1998 and 2012. As indicated by the low R value and the large P value, no significant correlations were found between SO_2, NO_2 and CO in 1998, which was consistent with biofuels to be the major source of the primary gas pollutants at that time. With the usage of fossil fuels and increasing consumptions, the concentrations of SO_2, NO_2 and CO increased dramatically and correlated more significantly with each other.

In response to increasing precursor emissions, the secondary gas pollutant O_3 generally experienced an enhancement in summer in Lhasa (Fig. 7b and c). The average increments of O_3 concentrations from June–September 1998 to June–September 2012 were respectively about 10, 6, 23, 14 ppbv in the afternoon (12:00–17:00 LST), which is the most productive period for O_3 photochemical formation during a day. The buildup of O_3 before the daily maximum in the afternoon (around 14:00 LST) was more efficient in summer 2012 than in summer 1998, accompanied by a higher level of O_3 peak in summer 2012. This may imply a larger contribution is now made by O_3 photochemical formation to the ambient O_3 concentrations in the daytime, especially around the noon, compared to the condition several years ago. With increasing O_3 precursor emissions and sufficient ultraviolet radiation in this area, more attention should be given to O_3 photochemistry in the future. Averagely, an increase in nighttime O_3 concentrations provided an evidence of elevated O_3 background in this region, implying strengthened atmospheric oxidizing capacity in Lhasa. However, significant local emissions of NO and NO_2 from vehicular exhaust and incense burning occasionally resulted in almost complete consumption of surface nighttime O_3.

It was also worth noting that high O_3 spikes in short duration (within 1 h) were observed around the noon in June 2012 as shown in Fig. 9, while none in summer 1998. After excluding the possibility of artifact introduced by the instrument, it was believed that those high O_3 spikes were probably an indicator of highly spatial inhomogeneity

ACPD
14, 11787–11814, 2014

in air pollution in Lhasa, and as a result of polluted air parcels experiencing active O_3 photochemical production and happening to pass by the site. This phenomenon can also be found in other seasons. High O_3 basically came from the west, occurred after a violent wind shift and the following small wind, calm wind stage. Sometimes, an increase in CO concentrations could also be observed when O_3 spike appeared. This suggested a strong photochemical origin of O_3. To thoroughly investigate this issue, especially the cause of the large O_3 difference, more measurements and analysis need to be carried out in the future.

4 Summary

Various gas pollutants including O_3, NO_x, CO and SO_2 were continuously measured from June 2012 to May 2013 at an urban site in Lhasa, Tibet. The seasonal variations of O_3 and O_x displayed a low valley in winter and a peak in spring, when the meteorology favored O_3 photochemical production. The maximum monthly mean concentrations of O_3 and O_x were observed in May, respectively as 56.8 ± 10.1 ppbv and 70.1 ± 10.6 ppbv. The independence of O_3 concentrations on wind speed and wind direction in spring and summer suggested an important role of photochemistry in the observed concentrations of this secondary pollutant, while in autumn and winter, the transport process made a major contribution, showing an increased O_3 concentrations under larger wind speed. Generally, O_3 concentrations in the SW–NW sector were nearly 10 ppbv higher than that in other directions in autumn and winter. The diurnal cycle of O_3 concentrations averagely exhibited a shallow flat peak for about 4–5 h in the afternoon and a minimum in the early morning throughout the year.

Concentrations of primary gas pollutants peaked from November to January with a large variability as 2.72 ± 2.05 ppbv for SO_2, 570 ± 300 ppbv for CO and 29.58 ± 16.16 ppbv for NO_x. In the rest of the year, SO_2, CO and NO_x averaged 0.77 ± 0.61 ppbv, 363 ± 94 ppbv and 17.10 ± 6.19 ppbv, respectively. A sharp decrease in the concentrations of primary trace gases was observed when wind speed increased.

ACPD
14, 11787–11814, 2014

A slight dependence of trace gas concentrations on wind direction was found only under low wind speed. This implied local emissions of primary gas pollutants to be predominant in Lhasa. Diurnally, pronounced double peaks could be clearly identified in all seasons, as a result of enhanced traffic emissions in the rush hours as well as the diurnal variations of the boundary layer. Nighttime concentrations of primary gases were particularly high in autumn and winter when calm conditions usually happened. Under such circumstances, surface O_3 could sometimes be totally consumed by the high level of NO.

A comparison has been made for measured NO_2, SO_2, CO and O_3 from June to September between 1998 and 2012, in order to investigate the impact of rapid urbanization on air pollution in Lhasa. Concentrations of NO_2, SO_2 and CO have greatly increased in the past 15 years, due to a marked increase in their emissions. This was resulted from a substantial growth in the demand of energy consumption in the city and a change in using fossil fuels instead of biofuels, which was also supported by the correlations among the primary gas pollutants. The distinct double-peak diurnal cycle of CO observed in summer 2012 reasonably indicated the major emission source for primary gase pollutants to be vehicular exhaust, given that there was no apparent diurnal cycle in summer 1998. In response to increased precursor emissions in the process of urbanization, there was a more efficient buildup of O_3 concentrations in the morning and a higher peak in the afternoon in summer 2012 than in summer 1998. An enhancement in O_3 concentrations would be expected in the photochemically active atmosphere with the ever increasing O_3 precursor emissions. Therefore, measures should be taken to control emissions of primary gas pollutants in very near future in Lhasa, in order to reduce the occurrence of primary gas pollution events and mitigate the ozone problem.

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ACPD
14, 11787–11814, 2014

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ACPD
14, 11787–11814, 2014

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ACPD
14, 11787–11814, 2014

Table 1. The exceedance frequency (%) based on hourly average concentrations of trace gases in the four seasons.

Item Standard*	O_3 80 ppb	NO_x 50 ppb	CO 1000 ppb	SO_2 10 ppb
Spring	1.6	2.0	0.8	0
Summer	0.1	1.7	1.3	0
Autumn	0	10.9	6.5	1.9
Winter	0	10.8	10.4	3.9

* Here, we define a standard by ourselves instead of using the national air quality standard of China (GB3095-2012). In Lhasa, exceedance occurred scarcely according to the standards of GB3095-2012.

ACPD
14, 11787–11814, 2014

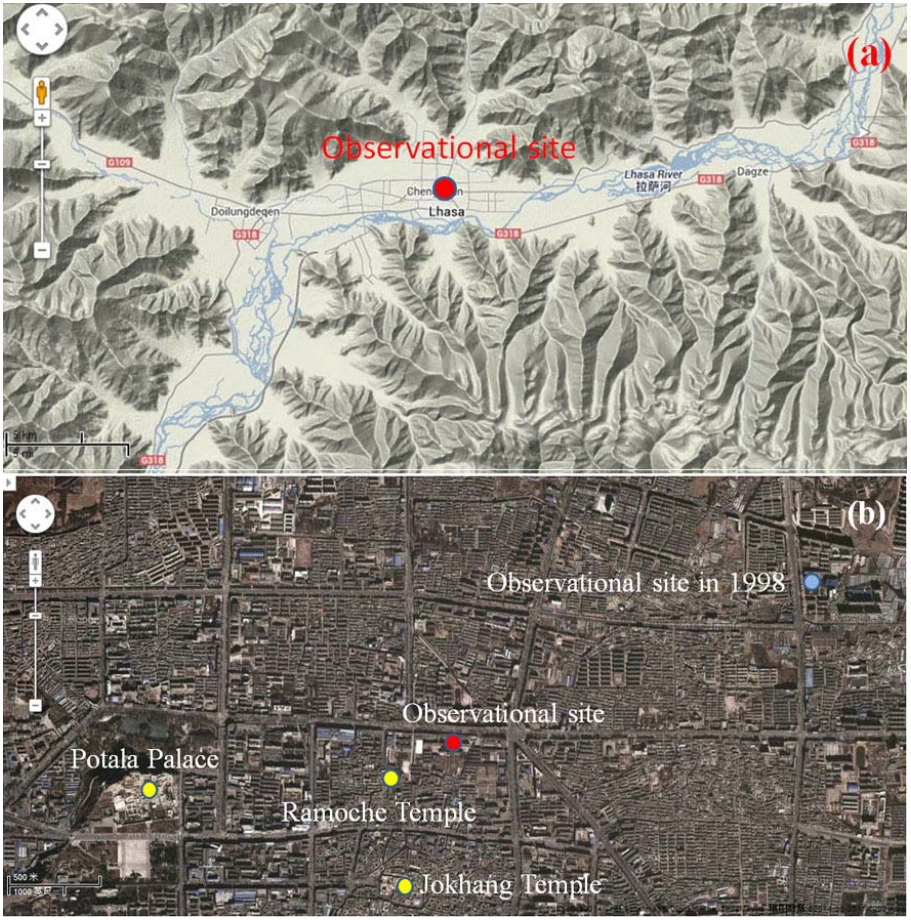

Fig. 1. (a) The topography and **(b)** the urban map of the site and its surrounding area (from Google Maps).

ACPD
14, 11787–11814, 2014

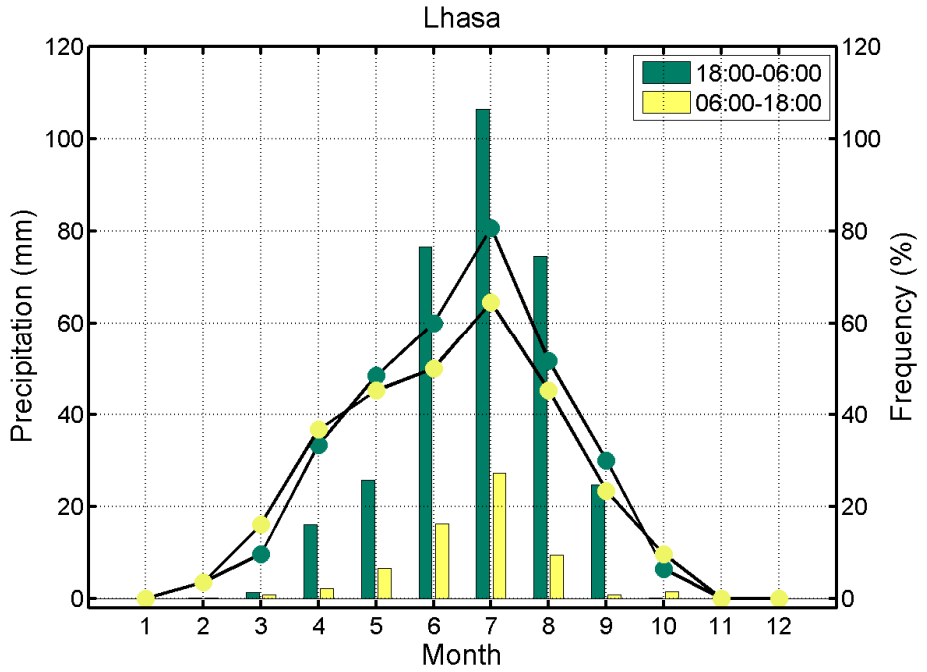

Fig. 2. Precipitation (bars) in the daytime (06:00–18:00 LST) and at night (18:00–06:00 LST) from June 2012 to May 2013 in Lhasa. The frequency of precipitation in each month is shown by dots.

ACPD
14, 11787–11814, 2014

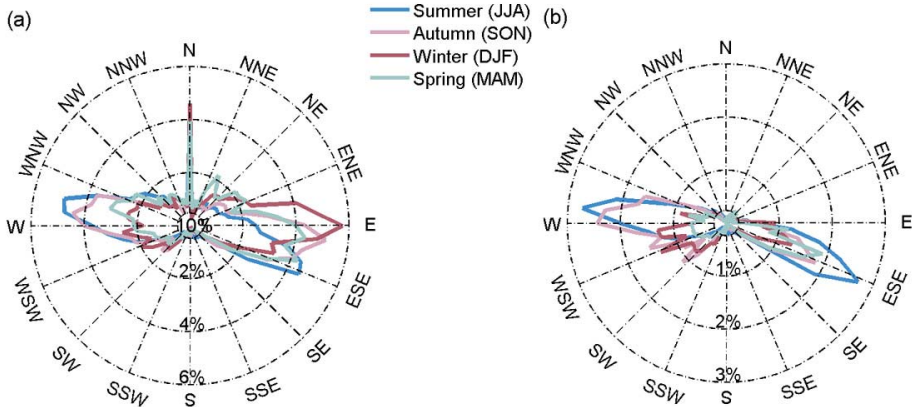

Fig. 3. The frequency of wind direction plotted by wind rose for four seasons in Lhasa, **(a)** with all wind speed, the frequency of calm conditions is given in the center circle, **(b)** with wind speed above 2 m s^{-1}.

ACPD
14, 11787–11814, 2014

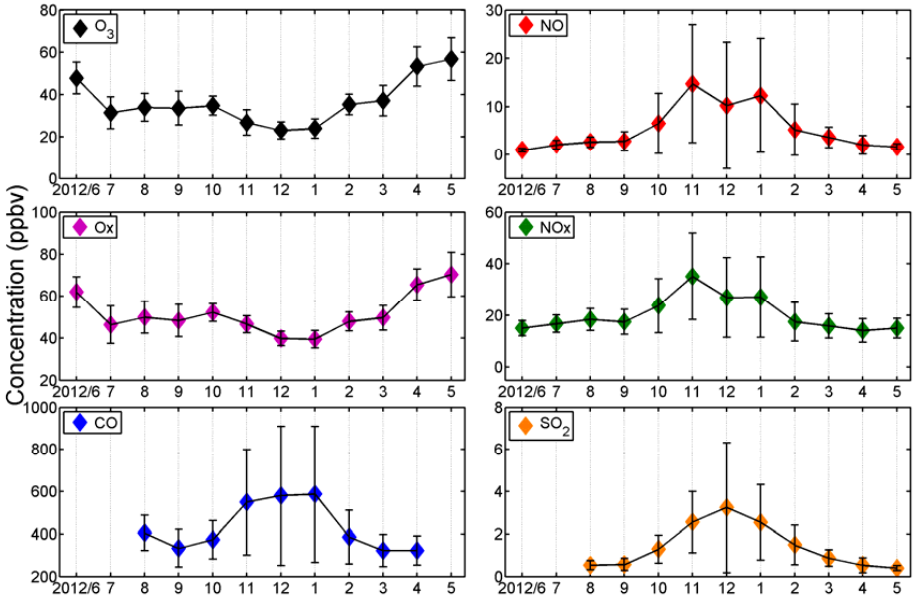

Fig. 4. Monthly averages (markers) and standard deviation (black lines) of gas pollutants in Lhasa from June 2012 to May 2013.

ACPD
14, 11787–11814, 2014

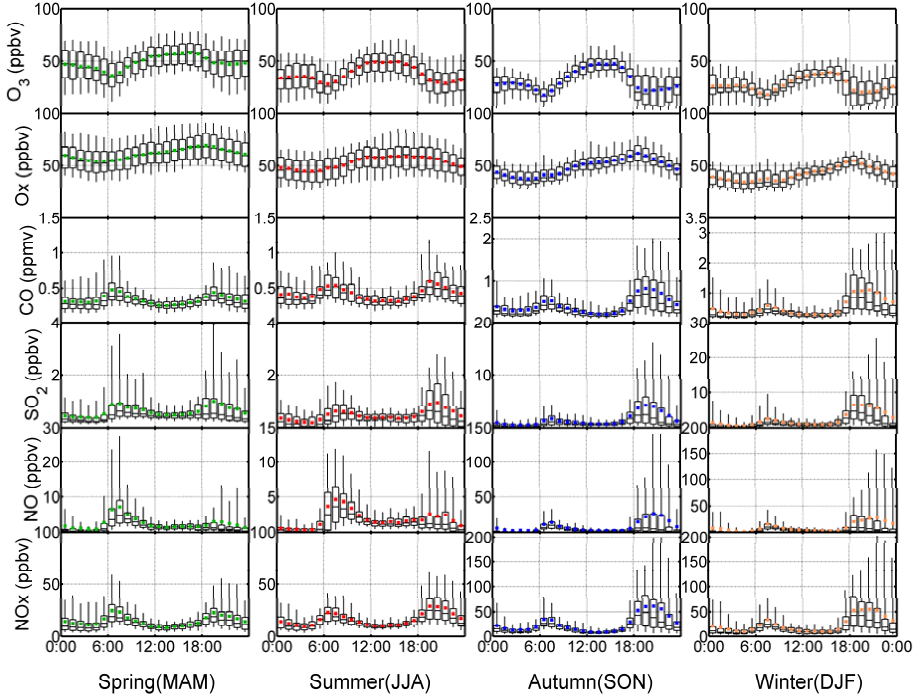

Fig. 5. Average diurnal variations of O_3, O_x, CO, SO_2, NO and NO_x concentrations in four seasons (during June 2012 and May 2013) in Lhasa. Colored markers represent hourly mean concentrations. Black boxes and whiskers indicate the 5th, 25th, 50th, 75th and 95th percentiles.

ACPD
14, 11787–11814, 2014

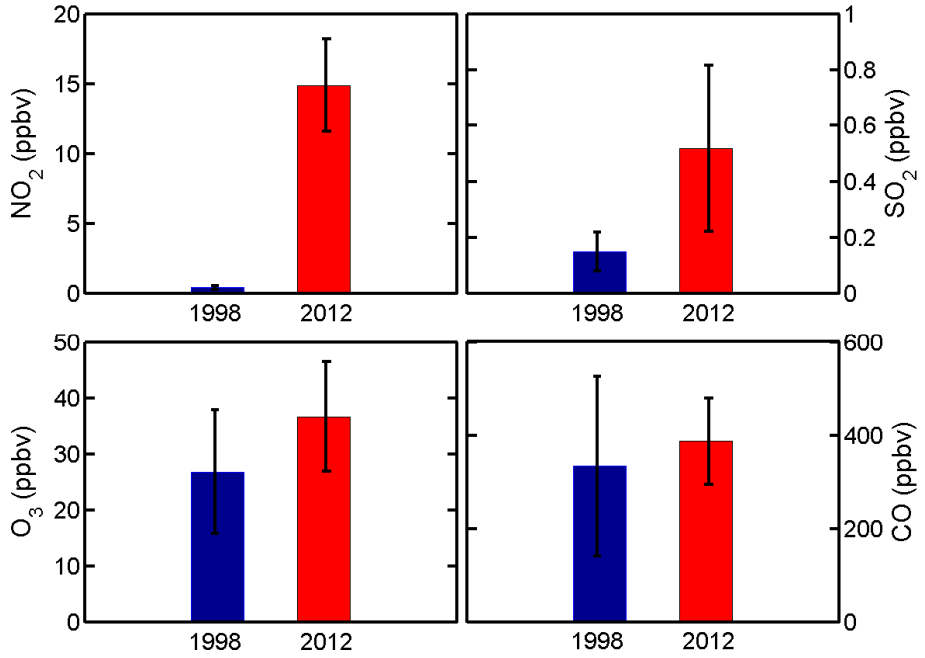

Fig. 6. Comparisons of the average concentrations (bars) of NO_2, SO_2, O_3, and CO during June and September between 1998 and 2012. The black line gives the standard deviation.

ACPD
14, 11787–11814, 2014

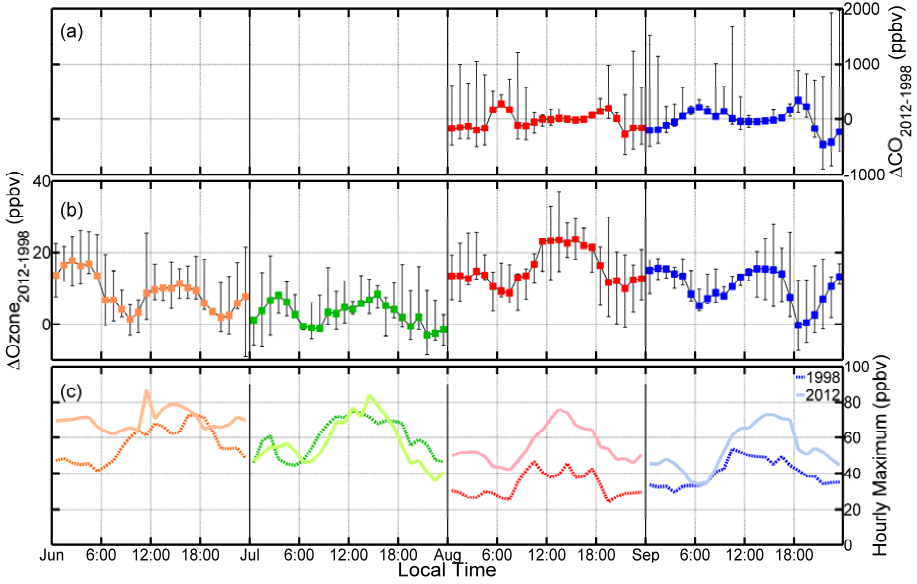

Fig. 7. (a) The differences in the average diurnal variations of CO concentrations between 1998 and 2012 in Lhasa, the dots represent monthly mean values, the black lines denote the minimum and maximum of the differences; **(b)** for O_3, the markers are the same as that in **(a)**; **(c)** the maximum O_3 concentration for each hour in each month, the darker color represents the values in 1998, whereas the lighter color represents the values in 2012.

ACPD
14, 11787–11814, 2014

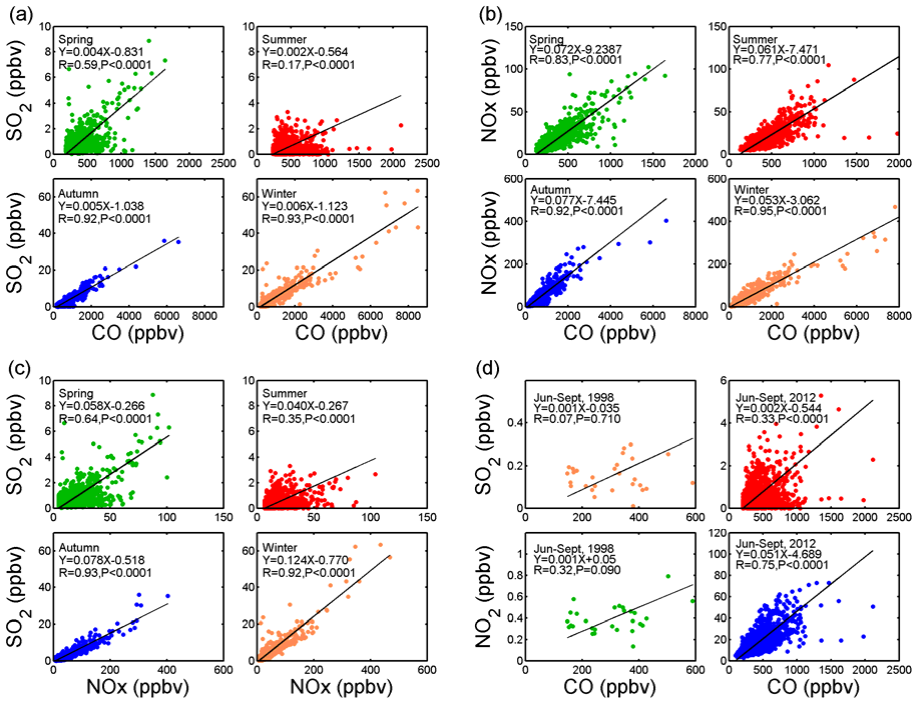

Fig. 8. Reduced major axis regression of **(a)** SO_2 vs. CO; **(b)** NO_x vs. CO; **(c)** SO_2 vs. NO_x in the four seasons during 2012–2013 in Lhasa using hourly average data. **(d)** Reduced major axis regression of SO_2 vs. CO and NO_2 vs. CO during June and September respectively in 1998 and 2012 in Lhasa.

ACPD
14, 11787–11814, 2014

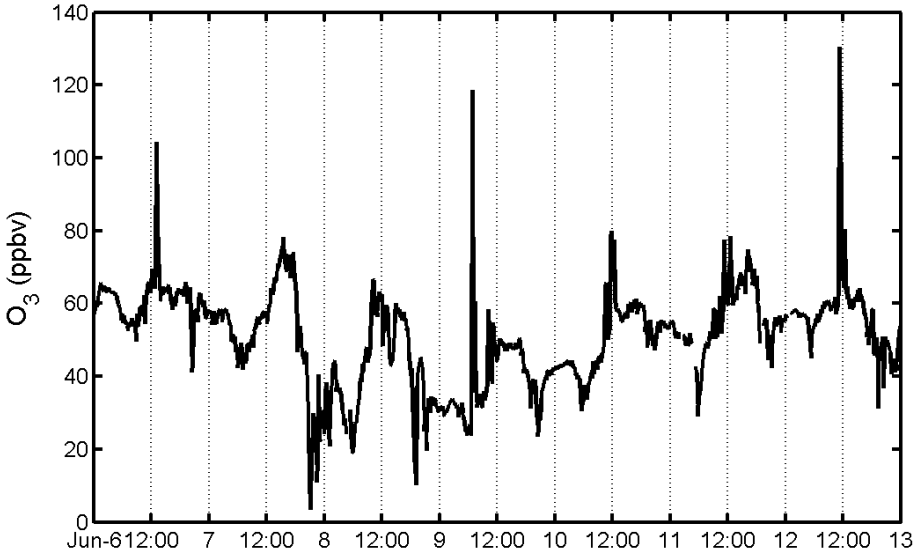

Fig. 9. High ozone spikes around the noon during 6 and 13 June 2012 in Lhasa.

ACPD
14, 11787–11814, 2014