Atmos. Chem. Phys. Discuss., 9, 8159–8185, 2009
www.atmos-chem-phys-discuss.net/9/8159/2009/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

Surface ozone trend details and interpretations in Beijing, 2001–2006

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Received: 12 March 2009 – Accepted: 19 March 2009 – Published: 27 March 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Beijing is a megacity situated in the rapidly developing Beijing-Tianjin-Hebei region of northern China. In this study, we analyze data on ozone and nitrogen oxide levels obtained at six urban sites in Beijing between the months of July and September. Our goal is to investigate average trends and interpretations over the 2001–2006 period. Average concentrations of NO_x (NO_x=NO+NO_2), O_3, and O_x (O_x=O_3+NO_2) were 49.2±5.9 ppbv, 26.6±2.8 ppbv, and 60.3±1.9 ppbv, respectively. NO_x concentrations decreased linearly at a rate of 3.9±0.5 ppbv/yr after 2002, while ozone concentrations increased at a rate of 1.1±0.5 ppbv/yr in a two-year cycle during 2001–2006, and O_x concentrations remained nearly constant. The reduction of NO_x emissions and elevated non-methane hydrocarbon (NMHCs) emissions may have contributed to the increased O_3 concentrations in Beijing. When the contributions from Beijings urban and surrounding areas were disaggregated via trajectory cluster analysis, daily maximum and average O_x concentrations attributable to Beijing local emissions increased linearly at rates of 1.3±0.6 ppbv/yr and 0.8±0.6 ppbv/yr, while the O_x concentrations attributable to regional areas decreased linearly at rates of 0.6±0.3 ppbv/yr and 0.5±0.3 ppbv/yr, respectively. The decrease in O_x concentrations of surrounding areas was found to counteract increasing Beijing urban O_x production, leading to nearly constant O_x concentrations in the Beijing region over the study period. Our results may be helpful for redefining government strategies to control the photochemical formation of air pollutants in the Beijing region. Our conclusions have relevance for developing megacities worldwide.

1 Introduction

Ozone is produced naturally both in the Earth's upper atmosphere and at ground level. Tropospheric ozone is both a greenhouse gas (Houghton et al., 2001) and an important source of global O_3 (Akimoto, 2003). Aside from these global effects, emissions

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of anthropogenic ozone precursors from urban and industrialized areas can elevate ozone concentrations in downwind suburban and rural areas (NRC, 1991). In addition, photochemical ozone is a key determinant of atmospheric oxidation state and a major constituent of photochemical smog, which impacts local air quality (Finlayson-Pitts and Pitts, 2000). The production of elevated levels of O_3 at ground level is of particular concern because ozone is known to have adverse effects on human health, vegetation, and a variety of materials (NRC, 1991; POPG, 1997). Along with accelerated urbanization, increases in surface ozone concentrations have been observed in areas throughout China (Xiaoyan, 1989, 1995; Zhang, 1998; Ma, 2000; Xu, 2008). Understanding the determinants of tropospheric O_3 formation in Beijing may help us better understand and forecast air quality in Chinese cities and around the globe.

Beijing has a population of 16 million within an area of 16 800 km^2, making it one of the largest and most densely populated cities in Northern China. Coal emissions and photochemical smog pollution have become increasingly serious with the rapid growth of Beijing's industrial sector since the 1980s. Zhang et al. (1998) began measuring O_3 concentrations at a single site in Beijing in 1982. The resulting time series reveals a marked increase in photooxidant concentrations over the 1982–1998 time period. Since 1998, pollution from the burning of coal has been reduced substantially (Zhang, 2006). However, skyrocketing land prices in the downtown area, accompanied by accelerated construction of commercial developments, have led to substantial urban sprawl and the migration of residential neighborhoods to peripheral districts. Changes in urban structure and in residents' lifestyles have increased the number of automobiles in the Beijing region (Beijing Municipal Bureau of Statistics, 2008). Photochemical air pollution from domestic sources has become increasingly problematic. Since Beijing's successful bid in 2001 to host the Olympic Games, the local government has gradually tightened the regulations that govern emissions from automobiles and from non-vehicular sources in the city. These changing regulations have produced rapid shifts in the spatial and temporal distributions of NO_x and NMHCs emissions in the city (Fig. 1). This situation offers us a meaningful context to investigate the relationships between

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O_3 and its precursors in an urban environment.

In this study, we illustrate the annual trends in atmospheric concentrations of O_3 and related components Beijing's urban areas during the period July 2001 until September 2006. A combined approach incorporating emissions inventories, meteorological data, and trajectory cluster analysis is used to evaluate factors influencing O_3 and O_x concentrations in Beijing and to identify strategies for controlling photochemical pollution in that city.

2 Methods

2.1 Data sources

Data were collected at six sites in downtown Beijing (Fig. 2). These sites are part of the Air Quality Monitoring Network established by the Institute of Atmospheric Physics (IAP). In order to focus on those months of relevance to the Olympic Games, ambient concentrations were recorded hourly throughout July, August, and September. In some cases, data were discarded due to equipment malfunctions, system failures, and power interruptions.

Surface ozone concentrations were measured using a Model 49 or 49C ozone analyzer from Thermo Environmental Instruments (TEI), Inc. NO_x levels were measured using TEI Model 42C and 42CTL NO and NO_2 analyzers. The TEI Model 49 detector was found to exhibit a detection limit of 2 ppbv and a precision of 2 ppbv, while Model 49C had a detection limit of 1 ppbv and a precision of 1 ppbv. Both NO_x analyzers had a precision of 0.4 ppbv, with detection limits for Model 42C and 42CTL of 0.4 ppbv and 0.05 ppbv, respectively.

Data quality was evaluated and certified by the China National Accreditation Board of Laboratories (CNAL), consistent with international requirements. IAP personnel strictly adhered to national environmental monitoring standards. Quality control checks including automatic zero-calibration and span checks of gas analyzers were performed daily,

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and manual calibrations with standard gases were conducted weekly. Sampling methods and instrument protocols, as well as quality assurance/quality control (QA/QC) procedures for air quality monitoring are described in detail in the Chinese National Environmental Protection Standard, Automated Methods for Ambient Air Quality Monitoring (HJ/T193-2005; State Environmental Protection Administration of China, 2006).

2.2 Total oxidant concentrations

We present a simplified scheme that describes photochemical reactions for O_3 and its precursors in Fig. 3. Atmospheric ozone at ground level is formed in the presence of UV light (λ<424 nm) through the direct photolysis of nitrogen dioxide. Nitrogen dioxide, in turn, is formed by the oxidation of nitric oxide, a species typically emitted from fossil fuel combustion (Seinfeld and Pandis, 1998). Two major pathways are known for NO_2 formation in urban atmospheres: NO oxidation either by O_3 or by peroxyl radicals produced by the photooxidation of non-methane hydrocarbons (Atkinson, 2000). In terms of the ozone pathway, it is clear that the O_3 production cycle (Fig. 3b) generates O_3, whereas the photo-stationary reactions (Fig. 3a) comprise a "do nothing cycle". In urban areas where O_3 precursors are present at sufficiently high concentrations, the radical pathway has been assumed to dominate, especially during summer months. However, the O_3 pathway remains important in areas that are associated with high NO_x emissions, even when the radical pathway dominates. Because NO_x emissions vary across time and space, the contribution of the O_3 pathway has prevented the accurate evaluation of O_3 levels and variability at certain sites. This phenomenon has also presented a barrier to comparisons of O_3 levels between sites with different NO_x concentrations (Kley et al., 1999).

In order to accurately measure the photochemical production of ozone, we followed the approach of Liu (1997) and defined "O_3+NO_2+ NO_z+O" as "total oxidant concentrations" (NO_z=NO_y−NO_x). In this study, we use "O_3+NO_2" as an estimate of total oxidant concentrations, because atomic oxygen is an ultra trace species in the troposphere, while NO_z species interfere with NO_2 measurements. The major advantage of

analyzing O_3+NO_2 in addition to O_3 is that O_3+NO_2 closely approximates total oxidant concentrations, and is therefore not affected by reactions between NO and ozone via the O_3 pathway. In other words, "O_3+NO_2" is a better measure of the true photochemical production rate of ozone.

2.3 Trajectory cluster analysis

To disaggregate the influence of local and regional contributions on air quality measurements in Beijing, we used a model to compute 2-day backward trajectories every 1h for the years 2001–2006 (Draxler and Hess, 1997) and cluster analysis was applied to all of our trajectories. Figure 4 displays the trajectory clusters for these six years. Our chosen sites in Beijing are predominately influenced by air masses from the south, consistent with the powerful effects of the Asian summer monsoon. Nearly 45% of the air masses reaching Beijing originate from the South, approximately 30% from Northern China, and 25% from the local area. These seven catalogs with different marks in Fig. 4 were generated and merged into two catalogs. The first catalog named Class I is marked with crosses (+) in Fig. 4b, denoting local pollutant concentrations and ignoring the influence of air masses from other regions. The second catalog named Class II takes into account the influence of air masses from other regions, including the rest six catalogs except Class I in Fig. 4, which represents net total pollutant concentrations due to both regional contributions and local emission sources. Using this method, local circulation and regional transportation are disaggregated and average concentrations of Class I and Class II are calculated (Table 2), standing for local and regional concentrations, respectively.

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3 Results and discussion

3.1 Comparison of pollutant concentrations at sites with different pollution characteristics

Table 1 summarizes pollutant data recorded from sites A1–A6 in July–September 2001–2006. NO_x concentrations at A1 exceeded those at A6 by more than 30 ppbv, while O_3 concentrations were lower at A1 than at A6. The potential for surface ozone production in the troposphere and at the boundary layer was found to be roughly equivalent across all of the 6 sites in downtown Beijing. However, differences in annual average ozone concentrations among the various sites were determined by taking into account differences in the rates of surface ozone elimination mechanisms at the respective locations. The A1 site, located in the center of Beijing, is generally exposed to greater concentrations of vehicular NO_x emissions. The reaction of more ozone with vehicular NO results in lower ozone levels at A1 than at the other sites, while lower combined NO_x emissions cause higher ozone levels at the A6 site. This inverse spatial relationship between ozone and NO_x levels is consistent with the findings of other groups (Bower et al., 1994; Mckendry, 1993; Helen, 2000; Charles, 2006). It is clear that site-to-site variability is closely related to site characteristics.

Figure 5a–b depicts the daily mixing ratios of O_3 and O_x for sites A1 and A6 in 2002. The differences between the O_x concentrations at these two sites were much smaller than the differences between the O_3 concentrations. Figure 5c shows scatter plots of O_x concentrations at A1 and A6. A first-order linear regression of O_x concentrations at these two points identified a strong correlation with a slope of 0.83. Possible explanations for variations in pollutant concentrations between different sites have been discussed by Clapp and Jenkin (2001). Explanations include variability in the fractional contributions of NO_2 to emitted NO_x, differences that might be linked to different vehicle fleet compositions, and different driving conditions around each site. Although both concentrations exhibit small site-to-site variations, O_x concentrations are thought to represent regional total oxidant levels better than O_3 concentrations.

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3.2 Annual trends

Figure 6a, b illustrates the trends in average annual concentrations of NO, NO_2, NO_x, O_3, O_3_max (daily maximum 1 h ozone), and O_x for the Beijing urban area during the period 2001–2006. The average concentrations of NO_x, O_3 and O_x are 49.2±5.9 ppbv, 26.6±2.8 ppbv, and 60.3±1.9 ppbv, respectively. Linear regressions show that concentrations of NO, NO_2, and NO_x decreased at a rate of 2.0 ppbv/yr, 1.9 ppbv/yr, and 3.9 ppbv/yr since 2002, respectively. Meanwhile, concentrations of O_3, O_3_max and O_x increased by 13%, 15% and 0%, respectively, over a two-year cycle period (with odd-year concentrations exceeding those for even years).

3.3 Annual trends of diurnal variability in O_3 concentration and in related precursors

Figure 7a–d illustrates the average diurnal variation in the hourly averages of NO_2, NO, O_x and O_3, respectively, in Beijing during 2001–2006. Maximum mean NO concentrations are observed between 07:00 h–08:00 h and at midnight (Fig. 7b). From 07:00 on, NO is converted to NO_2 via reaction with O_3, while NO_2 is converted back to NO during daylight hours as a result of photolysis, which also leads to the regeneration of O_3 (Jenkin and Clemitshaw, 2000). During the early hours of daylight, NO concentrations rise, mainly due to the increase in traffic. Figure 7a shows that the NO_2 production rates are greatest near 08:00 h (after dawn), a result that can be explained by reactions that involve NO and hydrocarbons (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998). After 08:00 h, [NO] diminishes until it reaches its lowest levels between 14:00 h–15:00 h (Fig. 7b). This NO decrease matches the increase in O_3 levels. The highest O_3 and O_x values are evident between 14:00 h and 15:00 h, after which O_3 and O_x levels decrease gradually (Fig. 7c–d). NO_2 decreases as O_3 increases, with rising concentrations after 15:00 h. NO increases with the onset of evening traffic, reaching its highest value between 01:00 h and 03:00 h. As NO reacts with O_3, ozone concentrations fall. Another factor that influences pollutant concentrations is the height of the

mixing layer over the city. From 08:00 h to 14:00–15:00 h, increasing global radiation and an increase in the height of the mixing layer (Ulke and Mazzeo, 1998) lead to a decrease in hourly NO_x concentrations and a trend toward increasing O_3. At night, low mixing layer heights may allow hourly NO_x concentrations to increase.

Figure 8b shows the annual changes in the daily morning average maximum of the relative diurnal variations of NO and NO_2. Daily morning average maximum values for NO and NO_2 decrease linearly at rates of 3.4 ppbv/yr and 2.5 ppbv/yr, respectively, after 2002, suggesting that mobile emissions of NO_x in Beijing may have decreased significantly over the period 2002–2006. Figure 8a shows the annual changes in the daily average maximum and minimum of the relative diurnal variations of O_x in Beijing. Maximum and minimum O_x concentrations changed linearly at rates of 1.0 ppbv/yr and −0.1 ppbv/yr, respectively. The increase in daily maximum [O_x] relative to constant daily minimum concentrations suggests increasing diurnal variations in ozone concentrations throughout Beijing.

From the above analysis, we arrive at two major conclusions. First, given that the morning maxima of NO and NO_2 concentrations reflect the mobile emission of NO_x, we conclude that the increasing daily minimum [O_3] is likely due to reactions with the decreasing daily morning [NO], accounting for the constant daily minimum [O_x] observed. Second, the changes of increase of the daily maximum [O_x], relative constant of the daily minimum [O_x] and increase of the daily amplitude of [O_x] reflect the enhanced local photochemical production.

3.4 Interpretation of concentration changes

3.4.1 Interpretation of ozone concentration changes

Concentrations of NO_x species, which are known O_3 precursors, decreased significantly after 2002 (Fig. 6a). However, over the same period, we also observed increased O_3 concentrations (Fig. 6b). Wakamatsu et al. (1996) reported worsening photochemical air pollution under conditions of decreasing concentrations of NO_x precursors in

metropolitan areas in Japan, and pointed to changes in the NMHCs/NO_x ratio as a possible explanation. In the absence of direct measurements of NMHCs concentrations, we use the emission ratio of NMHCs to NO_x in Beijing to explore this hypothesis. Figure 1 illustrates the increasing emission of NMHCs and the decreasing emission of NO_x in Beijing. Given the increasing emission ratio of NMHCs to NO_x, the observed trends of average and maximum [O_3] seem consistent with a system in which Wakamatsu's NMHCs/NO_x hypothesis describes the relationship between pollution controls and ozone formation rates.

3.4.2 Interpretation of total oxidant concentration changes

NO, NO_2, O_3, O_x and O_x_max were calculated for each year by local area and by region based on trajectory cluster analysis. While NO concentrations from all sources were nearly identical, NO_2, O_3, O_x and O_x_max concentrations in local air masses exceeded those of air masses from regional sources by more than 3 ppbv, 6 ppbv, 9 ppbv and 21 ppbv, respectively (Table 2). Figure 9a shows trends in the daily maximum and average concentrations of total oxidants in local air masses and 75th percentile concentrations of daily maximum aggregate total oxidants over the 2001–2006 period. In contrast to the nearly constant annual average concentrations of total oxidants (Fig. 6b), the maxima and average exhibit a significant upward trend with a slope of 1.3±0.6 ppbv/yr and 0.8±0.6 ppbv/yr, respectively (Fig. 9a). Because the highest 25% of concentrations were measured primarily at times when air masses originated from the Beijing urban area (Table 2), the 75th percentile concentration measurements also show an increasing trend at a rate of 1.2±0.5 ppbv/yr. Given the increasing emission of NMHCs and the decreasing emission of NO_x, an increasing photochemical production rate of O_x is to be expected. Therefore, the fact that total oxidant concentrations remained largely constant during the 2001–2006 period is of great interest.

The concentration of O_x at a given location is made up of two contributions: a regional contribution, equivalent to the background O_x concentration, and a local contribution that depends on the level of primary pollution in the area (Nicolas et al., 2005).

Considering the consistency between the trends of peak concentrations for oxidants and their precursors, we can infer that oxidant production from photochemical reactions in Beijing's local air masses likely increased during the 2001–2006 period. Hence, the contradictory observations of constant average oxidant levels over this period must be due to unknown factors that exactly offset this increased O_x production. The decrease in regional oxidant levels was identified as the most likely source of this phenomenon. The data in Fig. 9b suggest a decreasing trend in the daily maximum and average total oxidant concentrations from regional area sources. In terms of annual averages, the concentrations of daily maximum and average O_x decreased by 0.6±0.3 ppbv/yr and 0.5±0.3 ppbv/yr, respectively, during the 2001–2006 period. We speculate that decreasing regional background oxidant concentrations may have offset the increased oxidant local average oxidant production over this time period, accounting for the constant average oxidant levels observed.

3.4.3 Interpretation of the observed two-year cycle

In addition to precursor emissions, O_3 concentrations in urban areas are directly tied to meteorological conditions, such as maximum temperatures, solar intensity, precipitation, and stagnation. NRC (1991), Davidson (1993), and Wakamatsu et al. (1996) identified a positive relationship between ambient maximum temperature and daily maximum O_3 concentrations. Chun-ming (1994) also indicated that the absence of precipitation is a crucial parameter accompanying elevated noontime ozone levels. The relationship between the daily average maximum temperatures, total precipitation, and O_3 concentrations during 2001–2006 is shown in Fig. 10. A positive correlation is evident between the daily average maximum temperature and O_3 concentration, while increased precipitation is found to negatively impact O_3 production. These two factors appear to account for the observed two-year cycle of O_3 and O_x concentrations in Beijing.

4 Conclusions

This work aimed to identify the reasons for increased O_3 concentrations by analyzing the relationship between O_3 and its precursors. We tracked O_3+NO_2 in addition to O_3 because the former is approximately equal to the total oxidant concentration, and it can reveal regional atmospheric oxidation capacity better than O_3 alone.

We present annual trends in the concentrations of surface ozone and related components in Beijing. Our results suggest a decrease in average [NO_x] and an increase in average [O_3], with significant site-to-site variability. Our data also show a relatively constant average [O_x], with minimal site-to-site variability. Furthermore, we identified an increase in the daily amplitude of diurnal concentration variations, in the context of a two-year cycle for O_3 and O_x. All of these trends lead us to three major conclusions:

1. Beijing's surface ozone variability is accentuated primarily by a decrease in NO_x emissions and an increase in NMHCs emissions.

2. A decrease in regional O_x concentrations seems to counteract increasing local O_x production levels, and it leads to near-constant O_x levels in Beijing.

3. The influence of meteorological factors is the main explanation for the observed two-year cycle.

Increasing daily maximum ozone concentrations may exert negative impacts on human health and vegetation. Therefore, control measures should be taken to avoid further exacerbation of ozone pollution. Measures should include efforts to reduce NMHCs emissions.

Acknowledgements. This work was supported by a grant from the National Basic Research Program (No. 2007CB407303), the Knowledge Innovation Program of the Chinese Academy of Sciences (approved # KZCX1-YW-06-01), and the National Natural Science Fund (No. 40675073).

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Table 1. Summary of concentrations between 2001 and 2006 at six sites[a].

	A1	A2	A3	A4	A5	A6
Ave[b]						
NO_x	67	47	43	50	50	36
NO_2	42	33	31	34	33	28
O_3	22	30	30	22	25	32
O_x	64	63	61	57	58	60
Max[c]						
NO_x	151	115	100	119	119	81
NO_2	76	64	58	64	62	54
O_3	65	78	91	77	75	90
O_x	141	143	150	141	137	145

[a] Site descriptions correspond to those shown in Fig. 1;
[b] average concentrations in ppbv;
[c] 95th percentile concentrations in ppbv.

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Table 2. Disaggregated annual average results for each species[a].

	2001	2002	2003	2004	2005	2006	Avg[d]
Local[b]							
NO (ppbv)	12	20	17	16	14	11	15
NO_2 (ppbv)	32	41	38	36	35	33	36
O_3 (ppbv)	31	24	32	28	35	33	31
O_x (ppbv)	63	65	71	65	70	67	67
O_x_max (ppbv)[e]	95	97	102	95	103	102	99
Regional[c]							
NO (ppbv)	15	21	18	17	13	11	16
NO_2 (ppbv)	34	38	34	33	30	28	33
O_3 (ppbv)	25	21	26	24	30	26	25
O_x (ppbv)	59	59	60	57	60	55	58
O_x_max (ppbv)	80	78	79	78	79	76	78

[a] The concentrations of each species represents an average of measurements from all six representive stations in Beijing;
[b] Air masses from local area (Class I);
[c] air masses from regional area (Class II);
[d] average values during 2001–2006;
[e] daily maximum concentrations of O_x.

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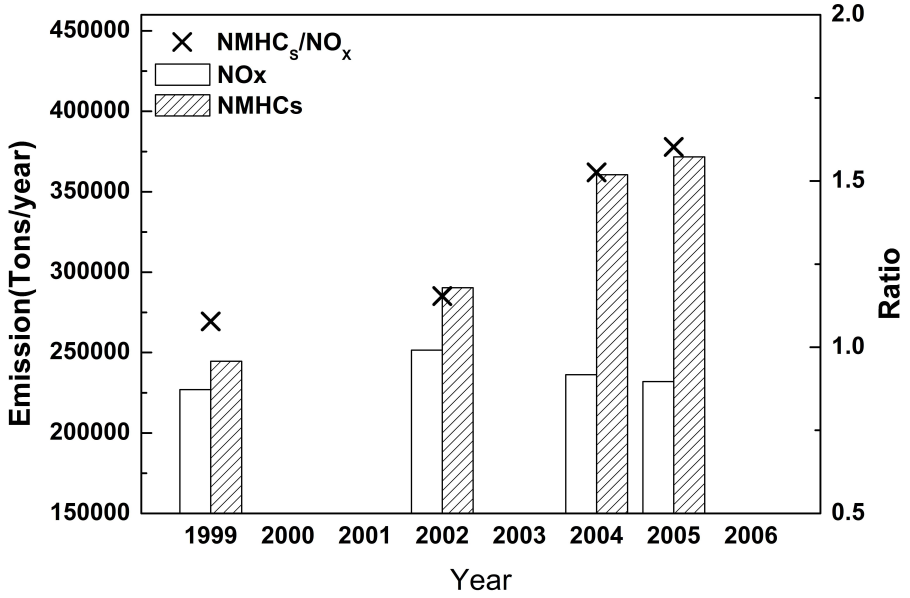

Fig. 1. NO_x and NMHCs emissions, and the ratio of NMHCs to NO_x in Beijing, 2001–2006. (National Science and Technology Department of Rural and Social Development Division, 2002; Beijing Municipal Environmental Protection Bureau, 2007; Beijing Municipal Environmental Protection Bureau, 2006; Tsinghua University, 2007).

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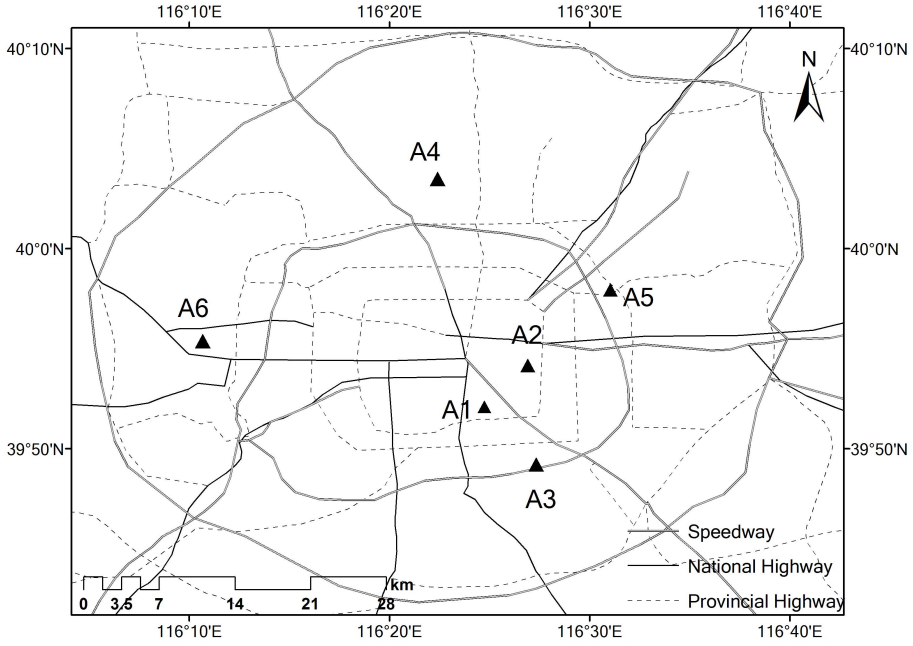

Fig. 2. Monitoring sites in Beijing, 2001–2006.

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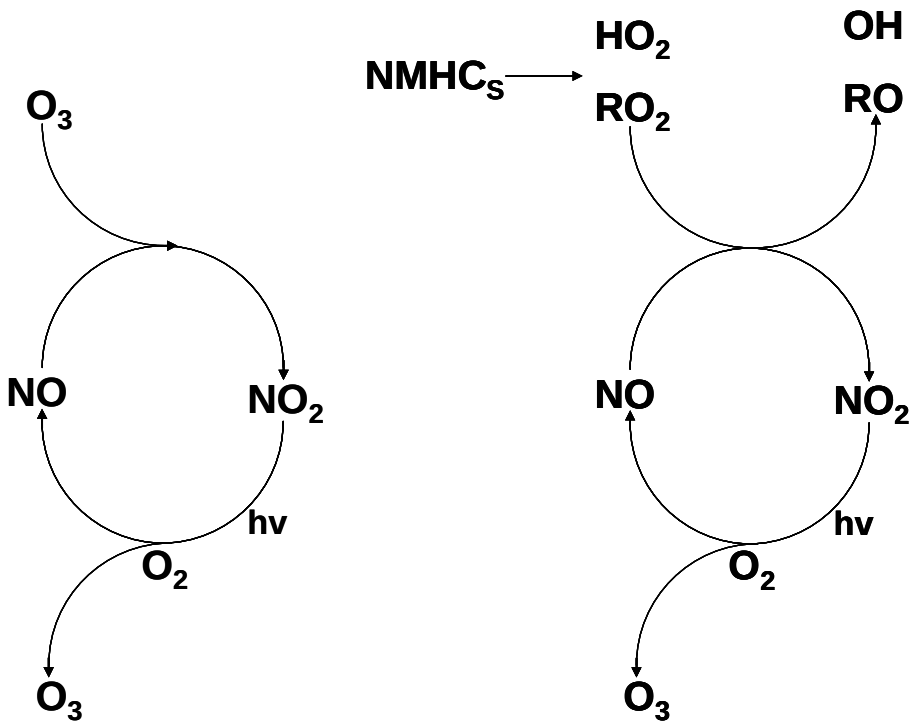

Fig. 3. Schematics of the reactions involved in NO-to-NO_2 conversion and O_3 formation in **(a)** NO-NO_2-O_3 systems in the absence of NMHCs, and **(b)** NO-NO_2-O_3 systems in the presence of NMHCs.

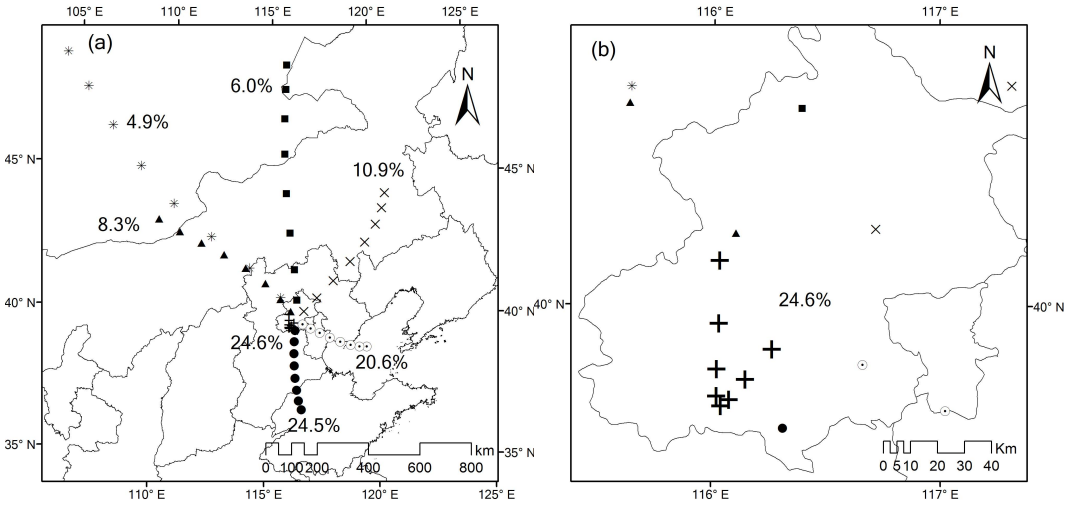

Fig. 4. Air mass backward trajectories for Beijing, **(a)** low resolution graph focused on the north of China, **(b)** high resolution graph focused on Beijing area. Trajectory clusters are calculated based on trajectories from 2001–2006. 48-h Trajectories are shown using 6-h steps.

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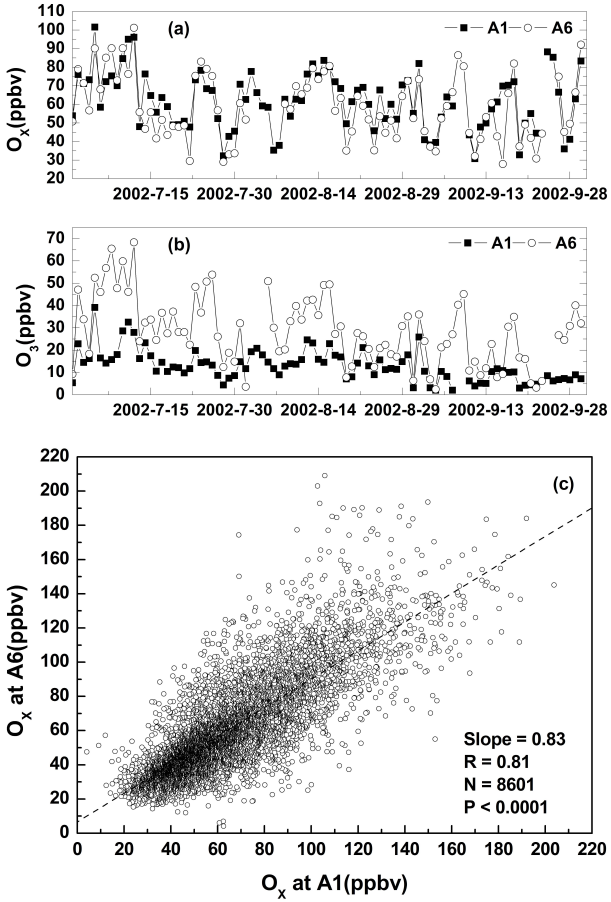

Fig. 5. Daily average concentrations of **(a)** O_x and **(b)** O_3 at sites A1 and A6 in 2002 and **(c)** the correlation between O_x concentrations at sites A1 and A6 during 2001–2006.

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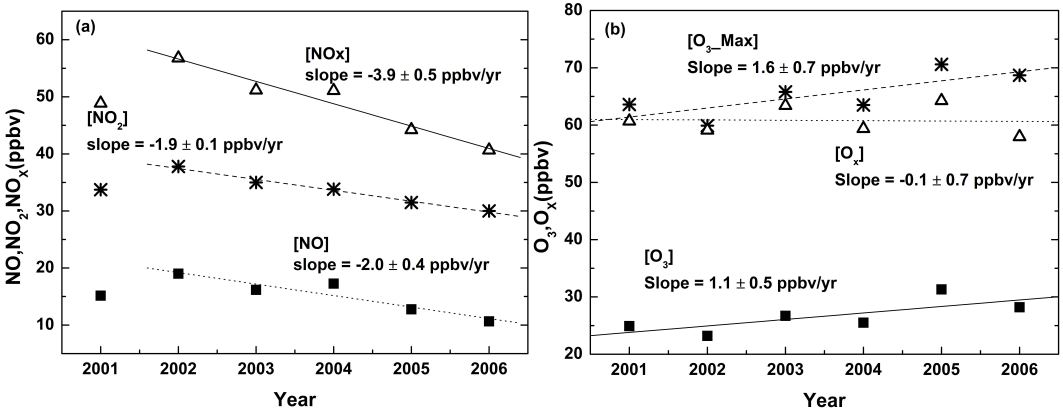

Fig. 6. Concentration trends for **(a)** NO, NO_2, NO_x, **(b)** O_3, O_x, 2001–2006. The concentration of each species represents an average of measurements from all six representative stations in Beijing.

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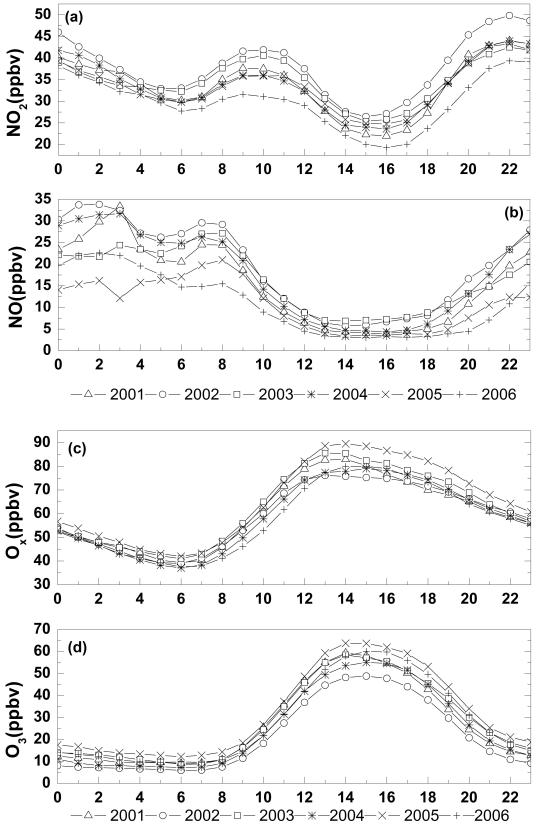

Fig. 7. Diurnal trends of NO **(b)**, NO_2 **(a)**, O_x **(c)**, O_3 **(d)**, 2001–2006. The concentration of each species represents an average of measurements taken from the six representative stations in Beijing.

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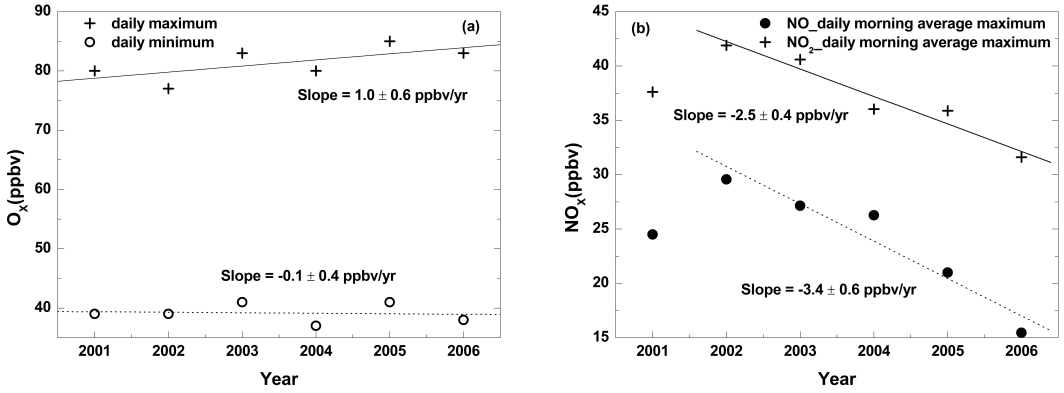

Fig. 8. Annual trends in the daily average maximum and minimum concentrations of **(a)** O_3 and **(b)** in the daily morning maximum concentrations of NO, NO_2, in 2001–2006. The concentration of each species represents an average of measurements taken from the six representative stations in Beijing.

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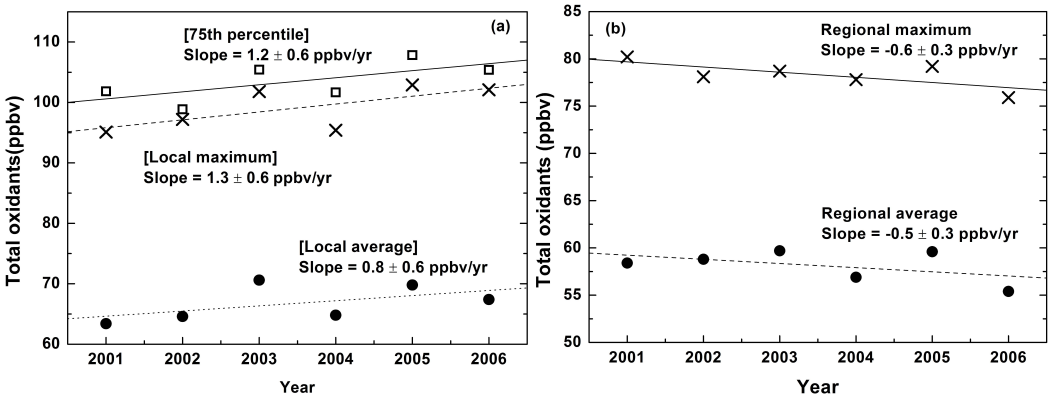

Fig. 9. Annual trends of **(a)** daily maximum and average total oxidant concentrations from local area sources (Class I) and 75th percentile daily maximum total oxidant concentrations from all sources, and **(b)** daily maximum and average total oxidant concentrations from regional area sources (Class II) during the 2001–2006 period. The concentration of each species represents the average of measurements across all six representative stations in Beijing.

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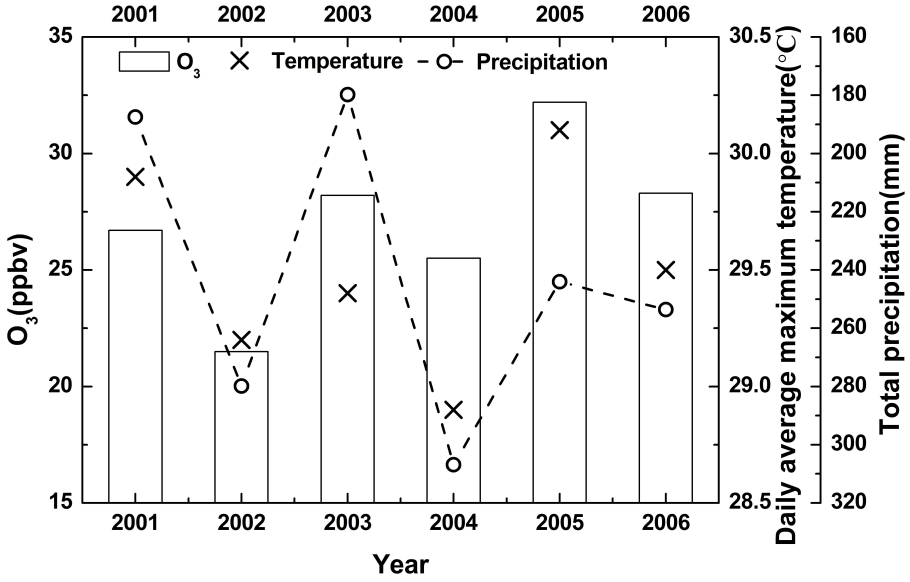

Fig. 10. Annual trends of daily average maximum temperatures, total precipitation and O_3 concentrations in July–September during 2001–2006.

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