



Results from the Mt.
Waliguan
Observatory

L. K. Xue et al.

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.

Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory

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Received: 13 March 2013 – Accepted: 16 April 2013 – Published: 2 May 2013

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The chemistry of the natural atmosphere and the influence by long-range transport of air pollution are key issues in the atmospheric sciences. Here we present two intensive field measurements of volatile organic compounds (VOCs) in late spring and summer of 2003 at Mt. Waliguan (WLG, 36.28° N, 100.90° E, 3816 m.a.s.l.), a baseline station in the northeast part of Qinghai-Tibetan Plateau. Most VOC species exhibited higher concentrations in late spring than in summer. A typical diurnal variation was observed with higher nighttime levels, in contrast to results from other mountainous sites. Five different air masses were identified from backward trajectory analysis showing distinct VOC speciation. Air masses originating from the central Eurasian continent contained the lowest VOC levels compared to the others that were impacted by anthropogenic emissions from China and the Indian sub-continent. The data were compared with the TRACE-P (Transport and Chemical Evolution over the Pacific) data to examine the inflow and outflow of air pollution over the China sub-continent. The results show that the free troposphere over China may be affected by the inflow from the Eurasian continent in spring, and the emissions in China may not have a significant influence on the free tropospheric outflow. A photochemical box model based on the Master Chemical Mechanism (version 3.2) and constrained by a full suite of measurements was developed to probe the photochemistry of atmosphere at WLG. Our results show net ozone production from in-situ photochemistry during both late spring and summer. Oxidation of nitric oxide (NO) by the hydroperoxyl radical (HO_2) dominates the ozone production relative to the oxidation by the organic peroxy radicals (RO_2), and the ozone is primarily destroyed by photolysis and reactions with the HO_x ($\text{HO}_x = \text{OH} + \text{HO}_2$) radicals. Ozone photolysis is the predominant primary source of radicals ($\text{RO}_x = \text{OH} + \text{HO}_2 + \text{RO}_2$), followed by the photolysis of oxygenated VOCs and hydrogen peroxides. The radical losses are governed by the self and cross reactions among the radicals. The findings can provide insights into the background chemistry and the impacts of pollution transport on the pristine atmosphere over the Eurasian continent.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

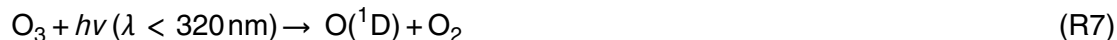


1 Introduction

5 Volatile organic compounds (VOCs) together with nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are key ingredients in the photochemical formation and fate of ozone (O_3) and other oxidants, which have great influence on atmospheric chemistry, regional air quality, and climate change (National Research Council, 1991; Crutzen, 1995). Tropospheric ozone originates primarily by downward transport from the stratosphere (Stohl et al., 2003), or from the in-situ photochemical production involving CO, VOCs and NO_x (Crutzen, 1973). In the lower troposphere, the photochemistry is more important than the stratospheric flux in controlling the ozone budget (Crutzen, 1995). The photochemistry can act as either a source or a sink for ozone, depending on the abundances of NO_x . In NO_x -rich environments, net ozone production can be achieved by the following simplified set of reactions:



20 While in the remote atmosphere where NO levels are very low, the photochemical production of ozone cannot compensate for those destroyed by photolysis (R7–8) and reactions with hydroxyl (OH) and hydroperoxyl (HO_2) radicals (R9–10), resulting in net ozone destruction.



11747

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





Given the dual roles of photochemistry in the ozone budget, it is of great importance to conduct concurrent measurements of NO_x , CO and VOCs in order to quantify the role of photochemistry in the background atmosphere in different regions of the world.

Long-range transport of air pollution can significantly influence the composition and chemistry of the natural atmosphere. Extensive efforts have been made to understand the long-range transport of Asian air pollution, driven in part by concerns of the rapidly increasing emissions of air pollutants from eastern Asia (e.g., Akimoto et al., 1996; Hoell et al., 1996 and 1997; Carmichael et al., 1998; Jaffe et al., 1999; Jacob et al., 1999). One of these efforts was the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) aircraft mission conducted in spring 2001, targeting the transport and chemical evolution of Asian continental air pollution over the Pacific Ocean (Jacob et al., 2003). Intercontinental transport of Asian pollution has been demonstrated to significantly affect the background levels of oxidants at the northern mid-latitudes (Berntsen et al., 1999), and have potential impact on the air quality over continents downwind (Jacob et al., 1999). However, there is little information about the westward transport of eastern Asian pollution and its impacts on chemistry of the remote atmosphere in the interior Eurasian continent. Moreover, there have been very few studies of the long-range transport of air pollution to East Asia from the upwind continents such as Europe (e.g., Wild et al., 2004). Consequently, it is necessary to consider these transport processes and understand their perturbation on the background atmosphere.

The Qinghai-Tibetan Plateau, located in the southwestern part of China, is the highest landmass on Earth, with an average altitude of over 4000 m above sea level (a.s.l.). Because of its unique geographic nature, the plateau is an ideal platform to study the chemistry of the background atmosphere and potential influences of pollution transport in the interior Asian continent. In 1994, China established its first (and to date the

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



only) continental baseline atmospheric observatory at Mt. Waliguan (WLG; 36.28° N, 100.90° E, 3816 m a.s.l.), located on the northeastern edge of the plateau in Qinghai Province (Tang et al., 1995). Since then, ozone, greenhouse gases and aerosols have been measured continuously along with complete meteorological parameters (Tang et al., 1995; Ma et al., 2003; Zhou et al., 2003, 2004; Kivekas et al., 2009). These observations have yielded invaluable insight into the composition and chemistry of background atmosphere in the Asian continent. However, there are few measurements of ozone precursors, in particular VOCs, which are emitted from both natural and anthropogenic sources (Ma et al., 2002). Such information would provide valuable chemical evidence of the origins of air masses in this pristine continental atmosphere.

An unresolved scientific debate is the origin of elevated summertime surface ozone over the northeast Qinghai-Tibetan Plateau. Ozone concentrations exhibited a broad summer peak at WLG (Tang et al., 1995), which contrasts with the common spring maximum pattern in most remote areas of the Northern Hemisphere (Monks, 2000). Many follow-up studies have debated whether pollution transport or stratospheric intrusion plays a more dominant role (Zhu et al., 2004; Ma et al., 2005; Wang et al., 2006; Ding and Wang, 2006; Li et al., 2009; Xue et al., 2011). An analysis of backward trajectories for summers from 2000-2009 suggests the dominance of transport of anthropogenic pollution from central and eastern China in most years, but also indicates considerable contribution of stratospheric intrusions (Xue et al., 2011). Another debate is on the role of in-situ photochemistry in the chemical ozone budget. Ma et al. (2002) applied a chemical box model to estimate the ozone budget at WLG and indicated a net destruction due to photochemistry in summer. In that study, ambient NO concentrations were not directly measured but estimated from filter-based measurements of NO₂. Subsequent in-situ measurements of NO implied a net ozone production (Wang et al., 2006). Evidently, a detailed analysis of the ozone chemical budget would need concurrent measurements of NO, CO and VOCs.

In April–May and July–August 2003 two intensive field studies, representing spring and summer seasons, were performed at WLG. A suite of air pollutants including O₃,

CO, NO, NO_y, VOCs, and meteorological parameters were measured. The measurement results of O₃, CO and NO_y during the campaigns have been reported by Wang et al. (2006). In this paper, we present the measurements of VOCs. We first show the temporal variations of various VOC species and make comparison with other remote stations at the northern mid-latitudes. We then apply the back trajectory techniques to classify the air parcels and examine the VOC speciation in different air masses. Finally, the observation data set is used to constrain a chemical box model to understand the photochemistry of this background environment including the budgets of ozone and radicals.

2 Methods

2.1 Observations

The field campaigns were carried out at the WLG Observatory, which is one of the World Meteorological Organization's (WMO) Global Atmospheric Watch (GAW) base-line stations. The Observatory has been used in many field studies, and has been described in detail elsewhere (e.g., Ma et al., 2003; Wang et al., 2006; Xue et al., 2011). Briefly, the station is situated on an isolated peak in the northeastern part of the Qinghai-Tibetan Plateau. It is relatively isolated from the industrialized and populated areas, with the population density less than 6 people per square kilometers (Zhou et al., 2003). The surrounding area has maintained its natural arid/semi-arid lands and scattered grasslands. The major anthropogenic emission sources nearby are located to the northeast and east (Fig. 1). Xi'ning, the capital of Qinghai Province, is about 90 km northeast of the station, with several high mountains (~4000 m a.s.l.) in between. To the east about 260 km is Lanzhou city, the capital of Gansu Province. A small town with a population of ~30 000 and light industry is located about 26 km to the west, and a few agricultural counties with very sparse population are located to the south.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Two phases of intensive measurements were conducted from 20 April to 22 May and from 15 July to 16 August 2003, which aimed to study the long-range transport from the west in spring and possible influences from the eastern Asia in summer. Two-liter electro-polished stainless steel canisters, previously cleaned and evacuated at the University of California, Irvine (UCI), were used for sampling VOCs. The sampling inlet was installed at 3 m above the rooftop of the station. During the sampling, whole air was drawn through a stainless steel tube by a metal bellows pump and pressurized into the canisters to 24 psig. After the campaign, the canisters were shipped to UCI's laboratory for chemical analysis. A 5-column multiple GC system equipped with flame ionization detection (FID), electron capture detection (ECD) and mass spectrometer detection (MSD) was employed to identify and quantify the VOCs species. Detailed descriptions of the canister preparation, chemical analysis, quality assurance and control, and measurement precision and accuracy for each species are given by Blake et al. (1994) and Simpson et al. (2010). Normally, two samples were collected each day, one at noon (~12:00 Local time, LT) and one at midnight (~00:00 LT), representing the well-mixed air masses in the planetary boundary layer and in the free troposphere, respectively. A total of 63 and 52 canister samples were taken during the spring and summer phases.

O₃, CO, NO and NO_y were continuously measured during the observation periods. The sampling system, instrumentation, calibration, measurement precision and uncertainties of these measurements have been described in detail by Wang et al. (2006). In addition, meteorological parameters including temperature, pressure, relative humidity, and horizontal and vertical winds, were routinely measured at the Observatory.

2.2 Calculation of backward trajectories

For high-elevation sites such as WLG, backward trajectory analysis is a useful tool to track the transport history of air masses sampled. In the present study, we utilized the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPPLIT, version 4.8) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (<http://ready.arl.noaa.gov/HYSPLIT.php>) to calculate

three-dimensional backward trajectories. The National Centers for Environmental Prediction (NCEP) FNL meteorological data were used as input. Considering the high wind speeds at mountainous sites and relatively short lifetimes of many VOC species, we chose to compute back trajectories for 5 days. Two trajectories were determined each day at the sampling hours with the ending points at 500 m above the ground of the station. The trajectories were then classified into different groups according to their origins and transport pathways. Finally, five groups of trajectories, representing different types of air masses, were extracted from the analysis.

2.3 Chemical box model

An observation-constrained photochemical box model was developed to probe into the chemistry of this background atmospheric environment. The model is configured based on the Master Chemical Mechanism (MCM, version 3.2; <http://mcm.leeds.ac.uk/MCM/>), which is a state-of-the-art chemical mechanism explicitly describing the degradation of 143 primary VOCs, comprising ~16 900 reactions of ~5725 organic species plus the latest inorganic mechanism from the IUPAC evaluation (Jenkin et al., 1997 and 2003; Saunders et al., 2003). In addition to this “complete” gas phase chemistry, heterogeneous processes regarding HONO formation and HO₂ loss were also taken into account in the model. We adopted the parameterizations of Li et al. (2010) for HONO formation from heterogeneous reactions of NO₂ on both ground and aerosol surfaces. As to losses of HO₂ on aerosols, the parameterization used by Edwards et al. (2011) was incorporated. The aerosol surface area concentration and area-weighted radius, two key parameters in both parameterizations, were not measured during our studies. They were derived based on the long-term measurements of aerosol number size distributions at WLG (Kivekas et al., 2009), and constant aerosol surface of $7.1 \times 10^{-5} \text{ m}^2 \text{ m}^{-3}$ and radius of $5.6 \times 10^{-6} \text{ cm}$ were used for both campaigns. Considering the facts that there was more anthropogenic influence (hence primary particles) at WLG in spring and at night but more extensive new particle formation (hence secondary particles) in summer and during the day (Wang et al., 2006; Kivekas et al.,

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2009), the assumption of constant aerosol surface and radius should be somewhat reasonable. It is also noteworthy that the related uptake coefficients are still quite uncertain and may be highly variable depending on temperature and aerosol components (Thornton et al., 2008; Li et al., 2010), hence sensitivity of the model output to these processes was tested (see Sect. 3.3.1).

The photolysis frequencies appropriate for WLG and the seasons were parameterized using a two stream isotropic scattering model under clear sky conditions, and were calculated as a function of solar zenith angle within the model (Hayman, 1997; Saunders et al., 2003). Sensitivity studies were performed to examine the effect of potential clouds and aerosols on the modeling results (see Sect. 3.3.1). Dry deposition velocities of various inorganic gases, PANs, peroxides, carbonyls and acids were adopted in the model from the recent compilation (Zhang et al., 2003). The mixing layer height was assumed to vary from 300 m at night to 1500 m in the afternoon in the base simulations. Sensitivity analyses with varying maximum mixing heights were also conducted (see Sect. 3.3.1).

In the present study, two sets of simulations were carried out for 1 May (spring phase) and 1 August 2003 (summer phase), respectively. The campaign-median diurnal profiles of O₃, CO, NO, methane, 35 major non-methane hydrocarbons (see Table 1 for the species), temperature, pressure, and relative humidity were used as inputs. The model was constrained every ten minutes by the measurement data to calculate the reaction rates of interest. For VOC species which were only measured at noon and midnight, the concentrations were assumed to be constant during the day (08:00–19:50 LT) and at night (20:00–07:50 LT), respectively. This should be reasonable according to the less-varied diurnal profiles of CO at WLG (Wang et al., 2006). Each simulation was performed for ten days to stabilize the intermediate products not prescribed in the model (e.g., radicals and OVOCs), and the output of the tenth day was used for the analysis. Therefore, the OVOC species were just simulated in the model with constraints of VOC precursors and were only of secondary origin. This should be also feasible for WLG which is a remote high-elevation site.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

3 Results and discussion

3.1 Temporal variation and comparison with other studies

3.1.1 Temporal variations

Table 1 documents the statistics of major VOC species measured at WLG during the spring and summer campaigns. Overall inspection of data revealed that the levels of VOCs were relatively low, indicative of the background nature of the atmosphere. Three different types of seasonal behaviors were found although the field measurements in the present study were only conducted in two seasons. A typical pattern with higher concentrations in late spring and lower values in summer was observed for most species. This is consistent with the seasonal trends of CO and NO_y during the same observations (Wang et al., 2006), and is also in line with other studies conducted in remote areas at the northern mid-latitudes (e.g., Rudolph, 1995; Atlas and Ridley, 1996; Klemp et al., 1997). Such patterns can be attributed to the seasonal variation of the atmospheric oxidative capacity, as confirmed by the higher levels of RO_x (RO_x = OH + HO₂ + RO₂) radicals in summer than in spring (see Sect. 3.2.2 and Fig. 7). For *i*-pentane and light olefins (i.e., ethene and propene), comparable and even slightly higher concentrations were detected in summer compared to those in spring. Given their relatively short lifetimes, this implied existence of local/nearby emission sources of these compounds with enhanced source strength in summer. Isoprene exhibited a pronounced pattern with much higher abundances in summer than in spring. This pattern is directly linked to the higher summertime temperatures, as the predominant biogenic source strength is known to increase with temperature (Guenther et al., 1997).

Figure 2 shows the diurnal variations of eight selected representative VOC species for both measurement campaigns. For combustion tracers (i.e., ethyne, benzene and methyl chloride (CH₃Cl)), and ethane and ethene, typical diurnal profiles of higher nighttime mixing ratios with lower daytime concentrations were determined. This pattern was also the case for most of the other species (figures not shown), and consistent

**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with the diurnal variations of CO during the same studies (Wang et al., 2006). Such diurnal variation of air pollutants is opposite to those observed at other mountainous sites, which generally show higher daytime and lower nighttime levels driven by the mountain-valley breezes (Zaveri et al., 1995; Fischer et al., 1998 and 2003; Zellweger et al., 2000; Carpenter et al., 2000). As a mountaintop site, WLG is also affected by mountain-valley breezes, with local anabatic and catabatic winds clearly observed during the observations (Wang et al., 2006; Xue et al., 2011). However, the daytime upslope flow of boundary-layer air and nighttime downslope flow of free tropospheric air resulted in a reversed diurnal variation of trace gases at WLG. This unusual phenomenon could be explained by transport of anthropogenic pollution during the night. This is illustrated by the diurnal variations of surface winds recorded at the Observatory, as shown in Fig. 1. In spring, the surface winds were mainly from the southeast or northwest with relatively low speeds in the morning, and became calm at noon when the daytime canister samples were collected. In the evening, the winds switched to the northeast/east directions with higher speeds till midnight when the nighttime samples were taken. A similar diurnal pattern of surface winds was also observed in summer. Therefore, transport of anthropogenic pollution from the northeast/east, where Xi'ning and Lanzhou are located, is likely responsible for the enhanced levels of CO and VOCs during the nighttime at WLG.

There were some exceptions to the aforementioned general diurnal pattern. Isoprene and *i*-pentane presented a diurnal profile with higher daytime and lower nighttime concentrations. For toluene and other reactive aromatics (e.g., ethylbenzene, xylenes and trimethylbenzenes; figures are not shown), the daytime concentrations were comparable to or slightly higher than those at night. These exceptions are consistent with the fact that the source strengths of these hydrocarbon species are stronger during the daytime since their emissions are related with temperature. *i*-pentane is usually recognized as a tracer of gasoline evaporation (Morikawa et al., 1998). The aromatic hydrocarbons are known as main components of solvent usage (Guo et al., 2006). Thus gasoline spillage processes and solvent usage activities in surrounding areas (maybe

the neighboring counties and town) should be important contributors to the relatively elevated daytime levels of *i*-pentane and aromatics at WLG.

3.1.2 Comparison with other mid-latitude remote locations

It is of interest to compare the levels of VOCs at WLG with those from other remote areas across the northern mid-latitudes. Table 2 summarizes the mean levels of major VOC species measured at WLG (this study, 3816 m), Jungfrauoch (Switzerland, 3580 m), Mt. Cimone (Italy, 2165 m), Mt. Tai (China, 1534 m), Happo (Japan, 1840 m), Mauna Loa (Hawaii, United States, 3400 m), and Izana (Spain, 2370 m). Jungfrauoch and Mt. Cimone are GAW stations in Europe, representing background conditions of the European continent. Mt. Tai and Happo are regional background stations in East Asia, with Mt. Tai located in the highly polluted region of the North China Plain (Suthawaree et al., 2010). Mauna Loa and Izana are representative high-elevation sites in the Pacific and Atlantic Oceans, respectively, and thus can reflect background conditions of the marine atmosphere.

Overall, the springtime VOC levels at WLG were significantly lower than those measured at Jungfrauoch. Compared with Mt. Cimone, the summertime levels of ethane, benzene, and ethyne at WLG were comparable or slightly higher. For short-lived species, however, the abundances at WLG were much lower, with the exception of isoprene that was influenced by local vegetation. This suggests a cleaner continental background condition of WLG than the European continent. Compared to WLG, much higher levels of VOCs were observed at Happo and in particular at Mt. Tai, indicating the strong influence of anthropogenic emissions from eastern China and Japan. In comparison, much lower VOC levels were observed at Izana and Mauna Loa, reflecting the fact that the marine atmosphere is less impacted by anthropogenic pollution and has clearer background conditions.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Influence of long-range transport

3.2.1 Air mass transport and VOC speciation

Transport of air pollution is an important factor affecting the chemical composition of air parcels at remote locations. In order to understand the impact of long-range transport on the measured VOC levels at WLG, we calculated 5-day backward trajectories corresponding to the VOC sampling, and derived five types of air masses for both campaigns according to the transport pathways of trajectories. Figure 3 shows the representative trajectories of the five air mass categories identified. Here we name them by the directions from which the air parcels originated, and make a brief description as follows. Type North, air masses originated from Siberia or Mongolia and passing over inland northern China in the lower troposphere; Type NW, air masses originated from the remote central Eurasian continent and traveling in the lower troposphere; Type NW-MT, air masses from the western/central Eurasian continent and traveling at high speeds in the middle troposphere; Type SW, air masses originated from India and climbing over the Qinghai-Tibetan Plateau; Type SE, air masses passing over southern and central China at lower altitudes before reaching the site. In spring, most of the samples corresponded with the air mass categories North (~40%) and NW (~32%), followed by NW-MT (~11%), SE (~10%), and SW (~8%). In summer, the sample distribution of air masses was: SE (~46%), NW (~33%), NW-MT (~12%), North (~6%), and SW (~4%). These transport patterns were consistent with those determined for the entire measurement campaign (Wang et al., 2006), and also agreed with the climatological summertime transport pattern of WLG (Xue et al., 2011).

The VOC speciation within different air masses was then evaluated. Considering the losses of VOCs during transport, here we only took into account the species with relatively long lifetimes (i.e. ≥ 5 days). Table 3 documents the statistics of CO and major long-lived VOC species in different air masses for both campaigns (Note that results were not obtained for Types North and SW in summer due to the low sampling frequencies.). Overall inspection indicated that the levels of CO and VOCs in air masses NW

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and NW-MT were much lower than those in the other three categories. It can be seen from Fig. 3 that NW and NW-MT mostly came from the lower and middle troposphere over the central Eurasian continent, a large remote region with very few anthropogenic emissions. Relatively higher VOC levels in Types North, SW and SE in spring indicated influences of anthropogenic emissions from specific regions over which the air parcels had passed. Here of interest is that the distributions in concentration of VOCs were different for the three air masses, although the levels of CO were similar. Type North contained the highest levels of ethane (1743 ± 348 pptv) and propane (343 ± 129 pptv), indicative of signature of natural gas leakage along the transport pathway. In comparison, Type SE had the most abundances of ethyne (548 ± 251 pptv), benzene (121 ± 46 pptv) and CH_3Cl (627 ± 42 pptv), which are primarily emitted from the combustions of fossil fuels or biomass. Both air masses also showed the highest concentrations of C_2Cl_4 ($9.5\text{--}9.6$ pptv), a tracer for urban or industrial activities (Wang et al., 1995). The mean mixing ratio of CH_3Cl (627 ± 23 pptv) in Type SW was among the highest, although the levels of other VOC species were relatively lower. CH_3Cl is usually recognized as a tracer for biomass/biofuel burning (Blake et al., 2003), so the results may reflect the importance of biomass/biofuel combustion in India or southwestern China.

3.2.2 Inflow and outflow of the China sub-Continent – comparison with the TRACE-P data

The springtime mean values of CO and long-lived VOC species in air mass types NW and NW-MT were then compared with those measured over the western Pacific during the TRACE-P aircraft mission in February–April 2001 (Russo et al., 2003). One purpose of this study was to examine the impacts of air pollution from the Eurasian continent on the sub-continent of China, whereas the focus of the TRACE-P mission was to understand the influences of Asian continental outflow (mainly from China) on the tropospheric chemistry over the downwind Pacific region. Thus, the comparison would provide insight into the pollution levels of air masses flowing into and out of the China sub-continent. Such information is critical to better understand the mechanism of

how the pollution emissions of China influence the chemical composition in the entire troposphere, and to assess the contribution of China to global air pollution loadings.

The comparison results are given in Table 4. Types NW-MT and NW indicate the inflow of air masses from the western/central Eurasian continent to the China sub-continent. The TRACE-P “Central” and “Coastal” represent the outflows (both in the free troposphere, i.e. >2 km, and in the boundary layer, i.e. <2 km) originating from the central (30° –60° N, 80°–130° E) and coastal regions (20°–40° N, 90°–130° E) of China (Russo et al., 2003). It can be seen that the mean CO levels (140–151 ppbv) in the free tropospheric outflow of China were somewhat higher than those measured in the inflows (111–133 ppbv). For the VOC compounds, however, the mean values observed in the outflows were comparable to those in the inflows. This implies that the free troposphere over the sub-continent of China may be influenced by the long-range transport of air masses from the Eurasian continent, but may not be influenced by the heavy surface pollution of China. This is consistent with previous studies in the western Pacific, which has found signals of European pollution in Asian continental outflow. For instance, the transport of European emissions was a possible cause of species enhancements at high altitudes over the western Pacific during the PEM-West B mission (Talbot et al., 1997). Anthropogenic emissions from Europe have been also found to contribute significantly to the Asian outflow at latitudes north of 40° N (Bey et al., 2001).

In comparison, the levels of CO and VOCs in the boundary-layer outflows were much higher than those in the inflows and also the free tropospheric outflows. This is a reflection that surface emissions from the China sub-continent were mostly concentrated in the boundary layer and could export to the downwind regions. Nonetheless, significant outflow of Asian pollution was occasionally encountered as far east as 150° E longitude and even in the middle and upper troposphere by the TRACE-P aircraft (Russo et al., 2003). In summary, this analysis of the measured data at WLG shows that the free troposphere over the China sub-continent is likely affected by the inflow from the Eurasian continent during spring. Emissions in China may not have significant influence on the

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



free tropospheric outflow, but may have a measurable impact on the boundary-layer outflow.

3.3 Daytime photochemistry

In this section, the daytime photochemistry of the natural continental atmosphere at WLG is explored with the aid of a photochemical box model constrained by a full suite of in-situ measurements (see Sect. 2.3). The issues of interest are: (1) what is the role of atmospheric photochemistry in the chemical ozone budget, and (2) what is the feedback of ozone on the atmospheric oxidation chemistry? Answers to these questions were probed by estimating the chemical budgets of ozone and RO_x radicals as described below.

3.3.1 In-situ ozone production

The in-situ photochemical production and destruction rates of ozone were calculated by the model. The ozone production is mainly achieved through the oxidation of NO by HO₂ and RO₂ (R3 and R4), and the production rate ($P(O_3)$) can be calculated as:

$$P(O_3) = k_4 [HO_2] [NO] + \sum (k_{3i} [RO_2]_i [NO]) \quad (1)$$

In addition to the photolysis and reactions with HO_x (HO_x = OH + HO₂) (R7–10), ozone can be also chemically destroyed by the reactions with unsaturated VOCs (R11).



Thus, the ozone destruction rate can be described as:

$$D(O_3) = k_8 [O(^1D)] [H_2O] + \{k_9 [OH] + k_{10} [HO_2] + \sum (k_{11i} [VOC_i])\} [O_3] \quad (2)$$

Then the net ozone production rate can be determined as the difference between (1) and (2).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Figure 4 shows the campaign-median diurnal variations of ozone production, destruction, and net rates at WLG calculated by the model. It can be seen that the ozone production was significantly greater than the ozone destruction during the daytime in both spring and summer, indicative of net ozone production in both seasons. The daytime average net production rates were estimated as 0.31 and 0.26 ppb h⁻¹ in spring and summer, respectively, indicating that 3.7 and 3.4 ppb of ozone can be formed from the in-situ photochemistry in the course of one day. Such amounts were of the same magnitude as the observed ozone increases of 4–5 ppb at WLG from the early morning to the late afternoon (Wang et al., 2006). Thus, the in-situ photochemical production should be an important factor in shaping the daytime accumulation of surface ozone at WLG. Our result is in disagreement with the previous modeling study by Ma et al. (2002) that suggested a net ozone production in winter but a net destruction in summer at WLG. The key to the difference between two studies is likely the levels of NO used in the models. In the work of Ma et al. (2002), NO was not in-situ measured but estimated in the model with constraints of NO₂ which was measured from the filter packs sampling and ion chromatography analysis. The filter measurements showed a NO₂ mixing ratio of 48 ppt with a model-simulated noontime NO level of 13–19 pptv in summer 1996. In comparison, our in-situ measurements suggested a much higher level of NO (40–50 pptv) in summer 2003. It is not clear whether the discrepancy in NO levels was due to the inter-annual variation of trace gas composition or the difference in the method for NO determination in the two studies. Accurate measurements of NO are critical to understanding the exact role of photochemistry in the ozone budget at WLG. Our result is also different from the chemical transport modeling study by Li et al. (2009), which derived a weak ozone destruction (–0.4 ppb day⁻¹) in summer at WLG.

The net ozone production rates determined at WLG in the present study are comparable to those deduced from other remote continental sites with similar NO levels. For instance, Fischer et al. (2003) reported a net ozone production rate of 0.1–0.3 ppb h⁻¹ at Mt. Cimone with mean NO levels of the order of 40 pptv during the June 2000 MINA-

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



TROC campaign. During the FREETEX'96 study at Jungfrauoch in April/May 1996, the daytime net ozone production rates were calculated as 0.27 and 0.13 ppb h⁻¹ by a photochemical box model and from the in-situ measurements of HO₂+RO₂ (Zanis et al., 2000b). During the following FREETEX'98 in March/April 1998, the experimentally derived net ozone production rates varied from ~0.1 ppb h⁻¹ for the relatively clean days to >1 ppb h⁻¹ on the more polluted days, with average NO levels of 27 and 261 pptv, respectively (Zanis et al., 2000a). By contrast, net ozone destruction was determined at Mauna Loa, a remote mountainous site in the central North Pacific with very low NO levels. During the MLOPEX2 campaign in 1991/1992, the net ozone production rates were estimated at -0.4-0.8 and -1.4 ppb h⁻¹ with mean NO levels of ~19 pptv in spring and summer, respectively (Ridley et al., 1998). Note that the North Pacific results are similar to those of Ma et al. (2002), who used similar NO input values.

Figure 5a and b break down the calculated ozone production and destruction rates from individual reaction pathways at WLG in late spring and summer. The partitioning of ozone production and destruction rates was similar in both seasons. Overall, the reaction of HO₂ with NO (R4) dominated the ozone production, with averages of 60 % and 52 % in spring and summer, respectively. The NO oxidation by RO₂ (R3) composed the remainder (40 % and 48 %), with CH₃O₂ alone making a considerable contribution (15 % and 20 %). In terms of ozone destruction, ozone photolysis (R8) contributed the most with means of 48 % and 54 % in spring and summer, followed by the reactions of O₃+HO₂ (R10; 36 % and 33 %) and O₃+OH (R9; 15 % and 11 %). The ozonolysis of unsaturated VOCs (R11) was only a minor contributor (1.4 % and 2.2 %) to the ozone loss due to the low levels of alkenes at WLG (see Table 1).

A number of sensitivity model runs were conducted to examine the sensitivity of ozone production to ozone precursors and to diagnose the modeling results against initial conditions. Figure 6a shows the responses of net ozone production rates to reductions by 20 % of CO, CH₄, non-methane hydrocarbons (NMHCs), and NO (note that only the summertime results are shown; the results in spring were similar). One can see that the ozone production at WLG was insensitive to CO, CH₄ and NMHCs,

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



but was highly sensitive to NO. A 20 % decrease in NO led to reductions of 28 % and 36 % in net ozone production in spring and summer. This was as expected that ozone production in remote atmospheres is generally in a NO_x-limited regime. Solar radiation affecting photolysis frequencies of various photo-sensitive species is an important factor in controlling the atmospheric photochemistry and thus ozone formation. In the base runs, the photolysis frequencies were parameterized with the assumption of clear sky conditions (no cloud and aerosol). Sensitivity tests by reducing photolysis rates by 20 % were carried out to examine the potential effects of cloud and/or aerosols on the modeling results. The results indicated that reducing photolysis frequencies could considerably cut down the net ozone production (13 % in spring and 10 % in summer; see Fig. 6b). Lowering photolysis can attenuate ozone production by reducing the supply of RO_x, which can be compensated in part by weakening the ozone loss by photolysis. Nevertheless, reduction in photolysis frequencies did not change the modeling conclusion that in-situ photochemistry led to net ozone production at WLG.

As the boundary layer height was not measured but assumed to vary within general values, sensitivity of the model output was tested by changing the maximum mixing height profiles (i.e., 1000 m and 2000 m). The results indicated that the impacts were negligible (<2 % of change in net ozone production rates). Given the important potential for the atmospheric oxidative capacity (e.g., Kleffmann et al., 1998; Thornton et al., 2008), the sensitivity of the model results to the heterogeneous processes of HONO formation and HO₂ loss were also tested by turning off these reactions and rerunning the model. The results were <5 % changes in the net ozone production rates. Hence these processes were found to be less important for the remote environment of WLG under conditions of very low concentrations of NO_x and aerosols.

3.3.2 Radical budget

Figure 7 depicts the modeled daytime profiles of OH, HO₂ and RO₂ at WLG for the spring and summer campaigns. As expected, the concentrations of HO₂ and RO₂ were significantly higher in summer than in late spring, although the OH levels were

comparable in both seasons. The midday peak mixing ratios of OH, HO₂ and RO₂ in spring were 0.26, 16.8 and 10.3 pptv, compared to 0.27, 22.5 and 18.9 pptv in summer. Such seasonal pattern of RO_x is linked with the seasonal behavior of most VOC compounds showing higher springtime and lower summertime concentrations. The peroxy radicals largely existed in the form of HO₂, which was also in line with the result that NO oxidation by HO₂ dominated the ozone production.

The simulated RO_x concentrations at WLG in this study were comparable to those derived from other remote mountainous sites at northern mid-latitudes. For example, at Mt. Cimone the measured average midday total peroxy radical (HO₂+RO₂) concentrations were of the order of 30 pptv during the MINATROC campaign conducted in June 2000 (Fischer et al., 2003). At Jungfraujoch, the mean midday levels of peroxy radicals were measured at 13 pptv during the FREETEX'98 in March/April 1998 (Zanis et al., 2000a). At Idaho Hill (USA, 3070 m), average noontime peroxy radical concentrations of 32 pptv were observed during the TOPHE campaign in August/September 1993 (Cantrell et al., 1997). At Mauna Loa, the intensive measurements during the MLOPEX2 in spring and summer 1992 showed average midday peroxy radical levels of 25 pptv (Cantrell et al., 1996). At Izana, the mean noontime concentrations of peroxy radicals were recorded at 65 pptv during the OCTA experiment in July/August 1994 (Fischer et al., 1998).

Table 5 documents the major initiation and termination processes of OH, HO₂, RO₂, and the total RO_x simulated at WLG. Overall, the budgets of RO_x radicals were similar in both seasons, although the reaction rates of most processes were much higher in summer than in spring. Ozone photolysis turned out to be the predominant primary source of OH and also RO_x with daytime average production rates of 172 and 274 pptv h⁻¹ in spring and summer, respectively. Photolysis of oxygenated VOCs (OVOCs) other than formaldehyde (HCHO) was the second largest source of RO_x mainly contributing to HO₂ (25.0 and 60.5 pptv h⁻¹) and RO₂ (31.7 and 67.7 pptv h⁻¹). HCHO photolysis was the third important source of RO_x, and also the largest source of HO₂ (48.4 and 89.6 pptv h⁻¹). The fourth important RO_x supplier at WLG was the

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



photolysis of hydrogen peroxides (H_2O_2) with average daytime OH production of 5.9 and 13.3 ppt h^{-1} in spring and in summer. Other initiation processes that may be important in polluted regions, such as HONO photolysis, ozonolysis of alkenes, and reactions of $\text{NO}_3 + \text{VOCs}$, contributed little to the primary RO_x production at WLG. The ultimate loss of radicals was dominated by the self and cross reactions among HO_2 , RO_2 and OH, which consumed RO_x on average at 196 and 384 ppt h^{-1} during the daytime in spring and in summer. In comparison, reactions of $\text{RO}_x + \text{NO}_x$ contributed only 48.5 and 37.1 ppt h^{-1} to the net radical losses during both campaigns. Furthermore, the heterogeneous loss of HO_2 on aerosols was negligible due to the very low aerosol loadings at WLG.

As indicated above, photolysis of ozone presents the predominant primary source of RO_x at WLG. This implies strong feedback of ozone to the photochemistry of this natural atmosphere. To quantify the impact of ozone on the atmospheric oxidative capacity, sensitivity model runs were conducted by reducing ozone levels to examine the response of RO_x production. The results are shown in Fig. 8. As expected, reduction in surface ozone (i.e., 20%) at WLG would result in significant decreases of the RO_x production rate (i.e., 14.5% in spring and 14.8% in summer). The ozone burden at WLG is primarily controlled by regional transport of photochemically produced ozone from the upwind regions (mainly central/eastern China), downward transport of stratospheric air, and in-situ photochemistry (Wang et al., 2006; Ding and Wang, 2006; Li et al., 2009). Our previous study indicated the dominant contribution of pollution transport from central/eastern China to the summertime surface ozone at WLG (Xue et al., 2011). The present study revealed a net ozone production from the in-situ photochemistry and positive feedback of ozone to the atmospheric photochemistry at WLG. These findings altogether suggest the strong perturbation of anthropogenic pollution transport from central/eastern China to the background atmosphere over the Qinghai-Tibetan Plateau, in terms of both chemical composition and inherent chemistry.

4 Summary and conclusions

Concurrent measurements of VOCs, NO, other related trace gases and meteorological parameters were made during two intensive campaigns in late spring and summer 2003 at WLG, a baseline observatory on the Qinghai-Tibetan Plateau. Most VOC species presented a seasonal pattern with higher springtime and lower summertime concentrations and a diurnal variation with higher nighttime and lower daytime values. During the campaigns, the site received air masses from the remote central Eurasian continent, from Mongolia and inland northern China, from central southern China, and from India and southwestern China, all of which showed distinct VOC speciation. The VOC levels in air masses coming from the west were compared with the TRACE-P data to investigate the pollution in the inflow and outflow of the China sub-continent. The results suggest that the free troposphere over China may be affected by the inflow from the Eurasian continent during the spring season. The analysis further indicates that surface emissions in China may not have significant influence on the free tropospheric outflow.

This study provided an opportunity to better understand the role of in-situ photochemistry in the chemical ozone budget at WLG, a topic currently still of some debate. Our results based on an observation-constrained photochemical box model suggest net ozone production due to the in-situ photochemistry in both spring and summer. This was different from the previous studies that suggested net ozone destruction in summer at WLG. Ozone was primarily produced by the oxidation of NO by HO₂ (and also RO₂), and was mainly destroyed via photolysis and reactions with OH and HO₂. The RO_x radical budget was also evaluated. Ozone photolysis was the predominant primary source of RO_x, followed by the photolysis of OVOCs and hydrogen peroxide. The radical loss was governed by the self and cross reactions of HO₂ and RO₂. The origins and photochemistry of VOCs obtained in the present study are useful to constrain/validate regional and global chemical transport models, and to yield scientific insights into the human perturbation of the natural atmosphere over this globally unique

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

landmass. Indeed, our findings (in combination with our previous studies) indicate that transport of anthropogenic pollution from central and eastern China can significantly perturb the chemistry of the background atmosphere over the plateau.

Acknowledgements. The authors would like to thank Steven Poon and Anson Wong for their contribution to the field studies. We are grateful to the staff at the WLG Observatory for their assistance throughout the field campaigns, to the Master Chemical Mechanism group in University of Leeds for providing the mechanism, and to NOAA Air Resources Laboratory (ARL) for providing the HYSPLIT model and meteorological data. The field measurements at WLG were supported by the Hong Kong Research Grants Council (PolyU5057/02E), and the data analysis was funded by the Norwegian Research Council (SOGG-EA, 193774) and the Hong Kong Polytechnic University (1-BB94).

ACPD

13, 11745–11788, 2013

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

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Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Hoell, J. M., Davis, D. D., Liu, S. C., Newell, R. E., Akimoto, H., McNeal, R. J., and Bendura, R. J.: The Pacific Exploratory Mission West phase B: February-March, 1994, *J. Geophys. Res.-Atmos.*, 102, 28223–28239, 1997.

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**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Results from the Mt.
Waliguan
Observatory**

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Table 1. Statistics of major VOC species measured at Mt. WLG^a.

| Species ^b | Spring (<i>n</i> = 63) | | | Summer (<i>n</i> = 52) | | |
|----------------------|-------------------------|----------|--------|-------------------------|----------|--------|
| | mean | σ | median | mean | σ | median |
| methane | 1.82 | 0.02 | 1.82 | 1.83 | 0.01 | 1.82 |
| ethane | 1532 | 308 | 1473 | 947 | 115 | 921 |
| propane | 279 | 111 | 259 | 147 | 45 | 137 |
| <i>n</i> -butane | 67.9 | 35.6 | 54.0 | 40.1 | 19.9 | 35.0 |
| <i>i</i> -butane | 54.7 | 44.8 | 40.0 | 30.2 | 18.2 | 27.0 |
| <i>n</i> -pentane | 22.1 | 14.2 | 16.0 | 16.9 | 10.1 | 14.0 |
| <i>i</i> -pentane | 63.4 | 56.6 | 39.0 | 68.8 | 81.5 | 40.0 |
| <i>n</i> -hexane | 9.9 | 7.2 | 8.0 | 7.1 | 7.3 | 6.0 |
| 2,2-dimethylbutane | 3.5 | 3.1 | 4.0 | – | – | – |
| 2-methylpentane | 11.1 | 13.3 | 6.0 | 13.3 | 10.4 | 10.0 |
| 3-methylpentane | 4.3 | 4.3 | 4.0 | – | – | – |
| <i>n</i> -heptane | 7.9 | 7.5 | 6.0 | 5.5 | 4.5 | 5.0 |
| <i>n</i> -octane | 5.6 | 6.1 | 4.0 | 5.7 | 2.2 | 5.0 |
| <i>n</i> -nonane | 6.0 | 7.1 | 4.0 | – | – | – |
| <i>n</i> -decane | 14.1 | 18.9 | 8.0 | – | – | – |
| cyclohexane | 4.4 | 3.1 | 4.0 | – | – | – |
| ethene | 131 | 145 | 95 | 138 | 111 | 97 |
| propene | 25.5 | 24.3 | 17.0 | 29.8 | 23.0 | 24.5 |
| 1-butene | 8.4 | 7.1 | 7.0 | 6.0 | 8.3 | – |
| <i>i</i> -butene | 21.3 | 36.2 | 11.0 | 8.6 | 9.6 | 8.0 |
| isoprene | 5.7 | 16.1 | – | 126 | 287 | 16.0 |
| ethyne | 392 | 204 | 358 | 293 | 182 | 232 |
| benzene | 86.5 | 47.1 | 76.0 | 67.8 | 41.8 | 56.6 |
| toluene | 184 | 275 | 76.0 | 62.3 | 62.5 | 49.5 |
| ethylbenzene | 24.0 | 40.4 | 8.0 | 7.1 | 6.1 | 6.0 |
| <i>m</i> -xylene | 69.1 | 137 | 14.0 | 14.1 | 10.2 | 10.0 |
| <i>p</i> -xylene | 50.9 | 110 | 6.0 | 2.7 | 3.3 | 1.5 |

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 1.** Continued.

| Species ^b | Spring (<i>n</i> = 63) | | | Summer (<i>n</i> = 52) | | |
|--------------------------------|-------------------------|----------|--------|-------------------------|----------|--------|
| | mean | σ | median | mean | σ | median |
| <i>o</i> -xylene | 45.7 | 81.4 | 10.0 | 9.4 | 7.4 | 8.0 |
| <i>m</i> -ethyltoluene | 6.8 | 12.1 | 3.0 | – | – | – |
| <i>p</i> -ethyltoluene | 3.8 | 6.9 | – | – | – | – |
| <i>o</i> -ethyltoluene | 3.1 | 5.9 | – | – | – | – |
| 1,2,3-trimethylbenzene | 14.7 | 23.6 | 6.0 | 5.7 | 4.9 | 4.0 |
| 1,2,4-trimethylbenzene | 21.8 | 36.1 | 9.0 | 5.9 | 4.8 | 5.0 |
| 1,3,5-trimethylbenzene | 10.1 | 15.9 | 6.0 | 2.6 | 2.7 | 3.0 |
| α -pinene | 6.8 | 7.6 | 4.0 | – | – | – |
| β -pinene | 6.7 | 7.8 | 5.0 | – | – | – |
| CH ₃ Cl | 599 | 37 | 591 | 552 | 33 | 540 |
| C ₂ Cl ₄ | 8.7 | 2.8 | 8.0 | 5.0 | 1.2 | 5.0 |

^aUnits are pptv, except for methane which is in ppmv. “–” denotes the values below detection limit.^bAll of these species were used to constrain the MCM box model.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Table 2. Comparison of major hydrocarbon levels at Mt. WLG with observations at other mountain sites^a

| Species | Waliguan ^b | | Jungfraujoch ^c | Mt. Cimone ^d | Mt. Tai ^e | Happo ^f | | Mauna Loa ^g | | Izana ^h |
|-------------------|-----------------------|-----------|---------------------------|-------------------------|----------------------|--------------------|-----------|------------------------|-----------|--------------------|
| | Spring | Summer | Spring | Summer | Summer | Spring | Autumn | Spring | Summer | Summer |
| Ethane | 1532 (308) | 947 (115) | 1755 (257) | 905 (200) | 2401 (778) | 1741 (670) | 749 (268) | 1027 (200) | 466 (121) | 501 (113) |
| Propane | 279 (111) | 147 (45) | 644 (981) | 268 (110) | 620 (331) | 613 (340) | 370 (219) | 76 (44) | 19 (11) | 52 (38) |
| <i>n</i> -butane | 68 (36) | 40 (20) | 159 (84) | 108 (68) | 209 (141) | 223 (101) | 103 (21) | 8.5 (10.6) | 1.5 (1.7) | 22 (31) |
| <i>i</i> -butane | 55 (45) | 30 (19) | 88 (52) | 96 (50) | 157 (87) | 131 (65) | 55 (14) | 4.5 (4.9) | 0.4 (6) | 14 (30) |
| <i>n</i> -pentane | 22 (14) | 17 (10) | 50 (37) | 35 (26) | 85 (53) | 81 (29) | 49 (9) | 1.8 (2.2) | 0.6 (0.3) | 14 (25) |
| <i>i</i> -pentane | 63 (57) | 69 (81) | 116 (108) | n.a. | 172 (96) | 112 (49) | 67 (15) | n.a. | n.a. | 14 (30) |
| Ethane | 131 (145) | 138 (111) | n.a. | 261 (120) | 994 (723) | 208 (86) | 296 (105) | 4.5 (1.7) | 3.5 (3) | 35 (20) |
| Propene | 26 (24) | 30 (23) | 52 (32) | 75 (39) | 110 (47) | 61 (19) | 101 (78) | 2.8 (1.2) | 1.9 (1.8) | 10 (4) |
| Isoprene | 6 (16) | 126 (287) | n.a. | 111 (124) | 173 (184) | n.a. | 343 (158) | 0.2 (0.6) | 0.7 (3.1) | 60 (124) |
| Ethyne | 392 (204) | 293 (182) | 567 (242) | 201 (102) | 1609 (969) | 696 (80) | 804 (471) | 231 (69) | 33 (22) | 52 (30) |
| Benzene | 87 (47) | 68 (42) | 148 (54) | 65 (33) | 641 (349) | n.a. | n.a. | 33.4 (17.7) | 7.1 (3.2) | 27 (24) |
| Toluene | 184 (275) | 62 (62) | 184 (156) | n.a. | 205 (123) | n.a. | n.a. | 1.1 (1.1) | 0.3 (0.3) | 26 (38) |

^aAll data are mean values (standard deviation) in pptv.

^bWaliguan: 36.28° N, 100.90° E, 3816 m a.s.l.; Spring: April 20 – May 22, 2003; Summer: 15 July–12 August 2003. This study.

^cJungfraujoch: 46.55° N, 7.99° E, 3580 m a.s.l.; Spring: 25 March–13 April 1998. Carpenter et al., 2000.

^dMt. Cimone: 44.18° N, 10.70° E, 2165 m. asl; Summer: June–July 2000. Fischer et al., 2003.

^eMt. Tai: 36.26° N, 117.11° E, 1534 m a.s.l.; Summer: June 2006. Suthawaree et al., 2010.

^fHappo: 36.68° N, 137.80° E, 1840 m a.s.l.; A whole-year measurement from March 1998–February 1999 was made. Sharma et al., 2000.

^gMauna Loa: 19.54° N, 155.58° E, 3400 m a.s.l.; Spring: 15 April–15 May 1992; Summer: 15 July–15 August 1992; Atlas and Ridley, 1996.

^hIzana: 28.31° N, 16.50° W, 2370 m a.s.l., Summer: 31 July–22 August 1993. Only daytime data are used. Fischer et al., 1998.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 3. Classification results of CO and selected long-lived VOCs in different air mass groups at Mt. WLG^a.

| Species | Spring | | | | | Summer | | |
|--------------------------------|----------------------------------------|------------------------|-----------------------|-----------------------|--------------------------|------------------------|------------------------|--------------------------|
| | North ^b (<i>n</i> = 20) | NW (<i>n</i> = 25) | SE (<i>n</i> = 6) | SW (<i>n</i> = 5) | NW-MT (<i>n</i> = 7) | NW (<i>n</i> = 17) | SE (<i>n</i> = 24) | NW-MT (<i>n</i> = 6) |
| CO | 153 (44) | 133 (27) | 152 (31) | 150 (21) | 111 (14) | 93 (9) | 125 (25) | 113 (24) |
| Ethane | 1743 (348) | 1427 (230) | 1560 (267) | 1547 (243) | 1266 (79) | 943 (100) | 949 (119) | 874 (107) |
| Propane | 343 (129) | 248 (69) | 334 (114) | 273 (122) | 166 (21) | 125 (35) | 167 (45) | 116 (30) |
| <i>n</i> -butane | 87 (42) | 60 (26) | 86 (30) | 59 (31) | 32 (7) | 27 (12) | 49 (22) | 34 (14) |
| <i>i</i> -butane | 62 (34) | 59 (60) | 64 (22) | 42 (25) | 20 (5) | 17 (8) | 39 (21) | 23 (13) |
| Ethylene | 443 (233) | 353 (165) | 548 (251) | 453 (140) | 214 (75) | 152 (67) | 370 (162) | 280 (129) |
| Benzene | 100 (61) | 76 (32) | 121 (46) | 99 (34) | 48 (14) | 35 (15) | 84 (36) | 65 (29) |
| CH ₃ Cl | 601 (40) | 589 (35) | 627 (42) | 627 (23) | 588 (16) | 539 (30) | 558 (29) | 559 (26) |
| C ₂ Cl ₄ | 9.6 (3.0) | 8.2 (2.6) | 9.5 (3.8) | 8.0 (2.8) | 7.4 (1.3) | 4.9 (1.1) | 5.1 (1.3) | 4.8 (0.8) |

^aValues are mean concentrations (standard deviation) in pptv; CO is given in ppbv.

^bSee text and Fig. 3 for the description of the air mass groups.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 4. VOC characteristics of continental inflow and outflow of the China sub-continent – comparison with the TRACE-P data^a.

| Species | WLG | | TRACE-P Central ^b | | TRACE-P Coastal ^b | |
|--------------------------------|------------|-----------|------------------------------|-------------|------------------------------|------------|
| | NW | NW-MT | 2–7 km | <2 km | 2–4 km | <2 km |
| CO | 133 (27) | 111 (14) | 140 (25) | 303 (153) | 151 (47) | 201 (107) |
| Ethane | 1427 (230) | 1266 (79) | 1415 (221) | 2695 (662) | 1085 (336) | 1498 (716) |
| Propane | 248 (69) | 166 (21) | 308 (96) | 1010 (586) | 171 (89) | 375 (448) |
| <i>n</i> -butane | 60 (26) | 32 (7) | 67 (30) | 290 (229) | 36 (30) | 121 (211) |
| <i>i</i> -butane | 59 (60) | 20 (5) | 40 (16) | 205 (231) | 23 (20) | 94 (160) |
| Ethyne | 353 (165) | 214 (75) | 339 (107) | 1465 (1639) | 376 (222) | 665 (749) |
| Benzene | 76 (32) | 48 (14) | 64 (25) | 431 (549) | 77 (55) | 189 (272) |
| CH ₃ Cl | 589 (35) | 588 (16) | 568 (23) | 654 (239) | 589 (32) | 638 (176) |
| C ₂ Cl ₄ | 8.2 (2.6) | 7.4 (1.3) | 6.0 (2.0) | 18.0 (19.0) | 5.0(2.0) | 9.0 (6.0) |

^aValues are mean concentrations (standard deviation) in pptv; CO is given in ppbv.

^bTRACE-P Central: 30°–60° N, 80°–130° E; TRACE-Coastal: 20°–40° N, 90°–130° E; refer to Russo et al. (2003) for detailed description of the source regions of Asian continental outflow.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

Table 5. Major Initiation and termination processes of RO_x radicals and their contribution as daytime averages at WLG^a.

| Chemical Process | Spring (07:30–19:30 LT) | | | | Summer (07:00–20:00 LT) | | | |
|---------------------------------------------------------|-------------------------|-----------------|-----------------|-----------------|-------------------------|-----------------|-----------------|-----------------|
| | OH | HO ₂ | RO ₂ | RO _x | OH | HO ₂ | RO ₂ | RO _x |
| Initiation pathways | | | | | | | | |
| O ₃ photolysis | 172 | | | 172 | 274 | | | 274 |
| HONO photolysis | 5.6 | | | 5.6 | 3.3 | | | 3.3 |
| HNO ₃ photolysis | 0.1 | | | 0.1 | 0.0 | | | 0.0 |
| H ₂ O ₂ photolysis | 5.9 | | | 5.9 | 13.3 | | | 13.3 |
| HCHO photolysis | | 48.4 | | 48.4 | | 89.6 | | 89.6 |
| other VOOCs photolysis | 4.2 | 25.0 | 31.7 | 60.9 | 8.0 | 60.5 | 67.7 | 136 |
| O ₃ + VOOCs | 1.5 | 0.3 | 1.3 | 3.1 | 2.6 | 1.8 | 1.1 | 5.5 |
| NO ₃ + VOOCs | | | 1.9 | 1.9 | | | 0.6 | 0.6 |
| HO ₂ NO ₂ photolysis ^b | | 0.0 | | 0.0 | | 0.2 | | 0.2 |
| Termination Pathways | | | | | | | | |
| OH + NO | 3.9 | | | 3.9 | 2.5 | | | 2.5 |
| OH + NO ₂ | 10.7 | | | 10.7 | 7.4 | | | 7.4 |
| OH + HO ₂ | 12.5 | 12.5 | | 25.0 | 19.0 | 19.0 | | 38.0 |
| HO ₂ + HO ₂ | | 65.2 | | 65.2 | | 134 | | 134 |
| HO ₂ + RO ₂ | | 52.0 | 52.0 | 104 | | 103 | 103 | 206 |
| HO ₂ heterogeneous loss | | 5.5 | | 5.5 | | 8.4 | | 8.4 |
| RO ₂ + RO ₂ | | | 1.6 | 1.6 | | | 6.4 | 6.4 |
| RO ₂ + NO = RONO ₂ | | | 4.4 | 4.4 | | | 4.0 | 4.0 |
| RO ₂ + NO ₂ | | | 29.5 | 29.5 | | | 23.2 | 23.2 |

^a Units are ppt h⁻¹.

^b The formation rate of HO₂NO₂ from HO₂ and NO₂ has been subtracted.

^c The formation rates of RO₂ from PANs decomposition have been subtracted.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Results from the Mt. Waliguan Observatory

L. K. Xue et al.

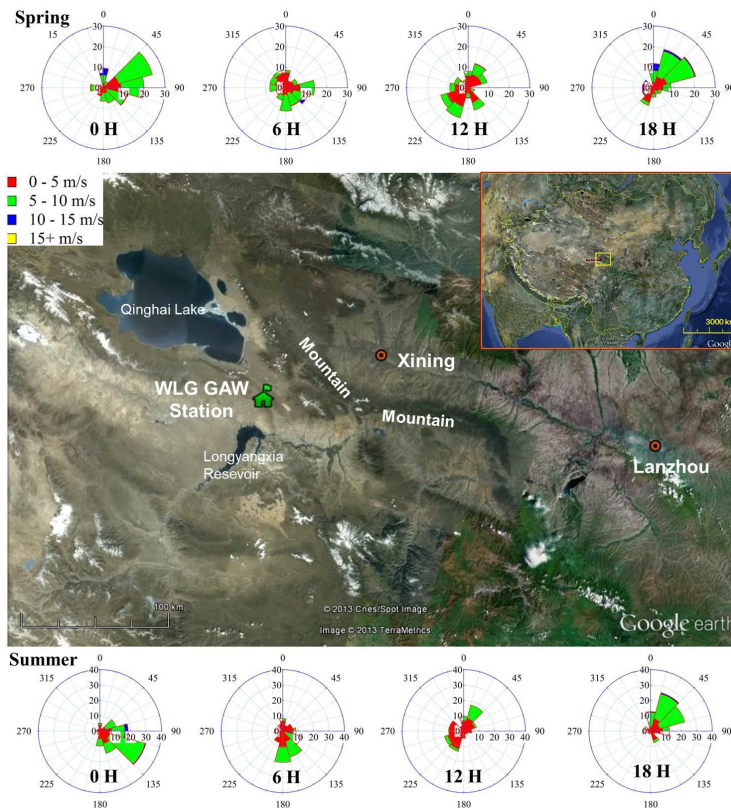


Fig. 1. Map from Google Earth showing the WLG Observatory and surrounding areas. The main figure is the zoomed view of the yellow box in the inner map. The diurnal variations of surface wind recorded in spring and summer were also shown.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



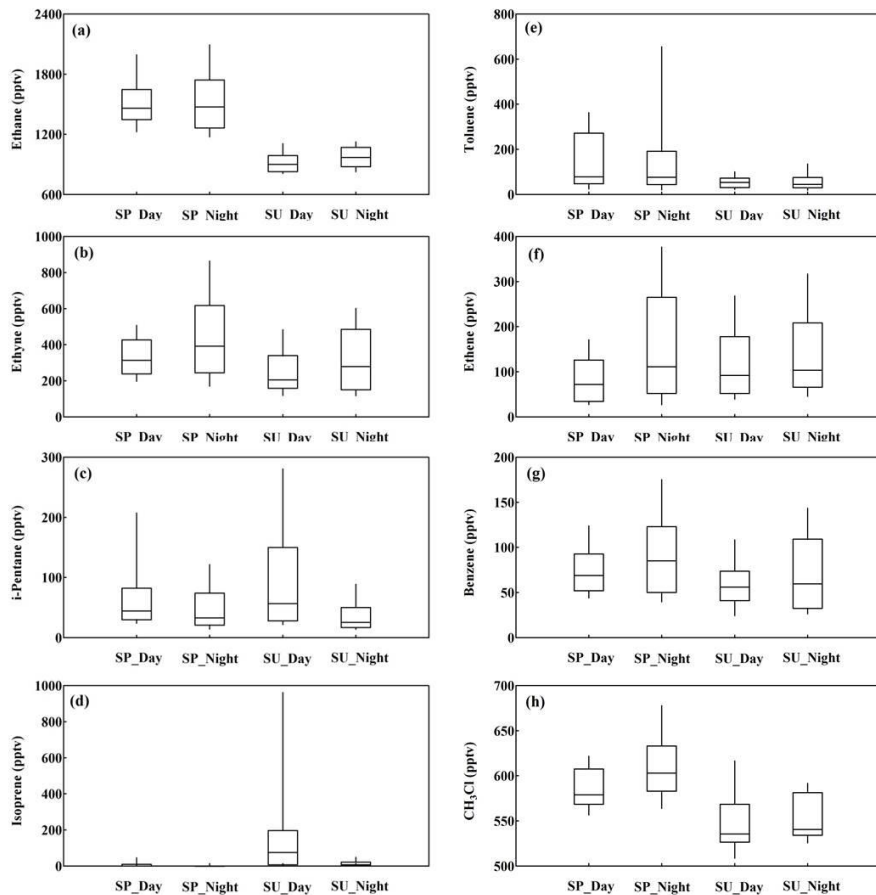


Fig. 2. Diurnal patterns of **(a)** ethane, **(b)** ethyne, **(c)** *i*-pentane, **(d)** isoprene, **(e)** toluene, **(f)** ethene, **(g)** benzene, and **(h)** CH₃Cl at WLG in spring (SP) and summer (SU). The box plot gives the 90%, 75%, 50%, 25%, and 10% percentiles of the measurement data.

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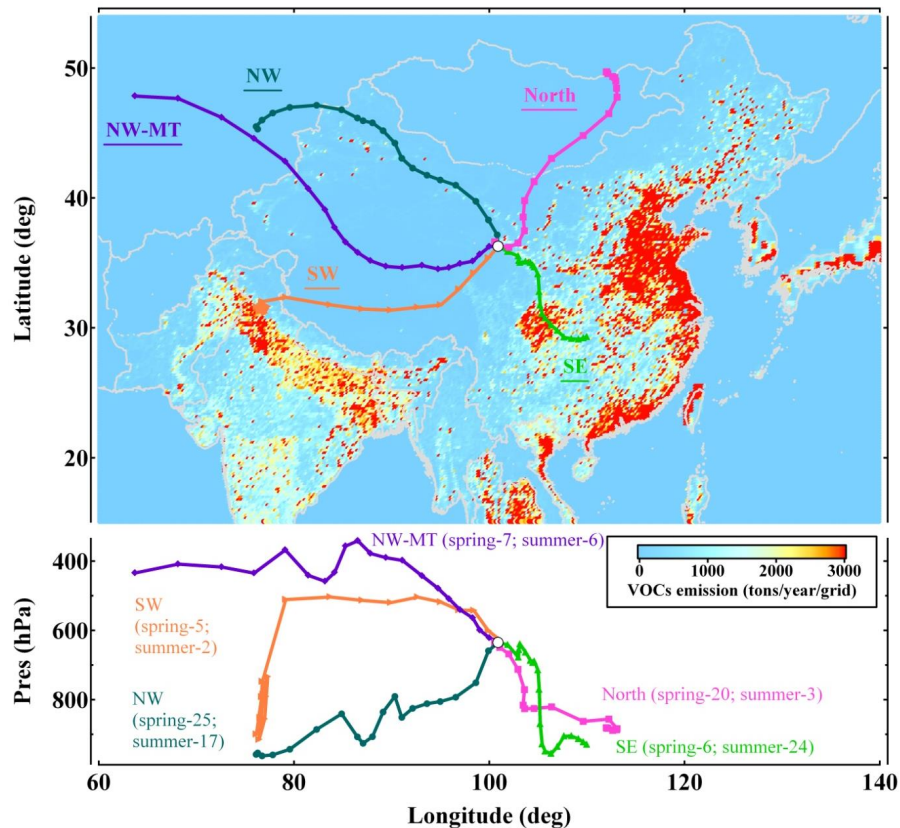


Fig. 3. Five types of air masses classified by the 5-d backward trajectories at WLG. The anthropogenic VOC emission data was provided by Zhang et al. (2009).

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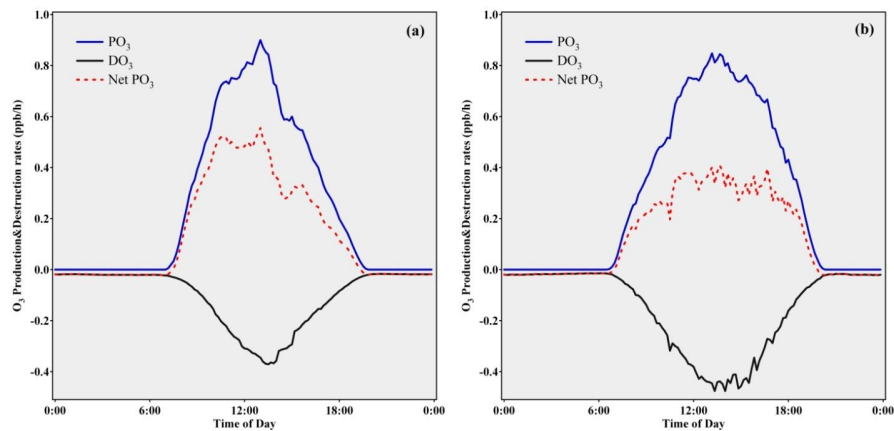


Fig. 4. Modeled O₃ in-situ production, destruction, and net rates at WLG in **(a)** spring and **(b)** summer.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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L. K. Xue et al.

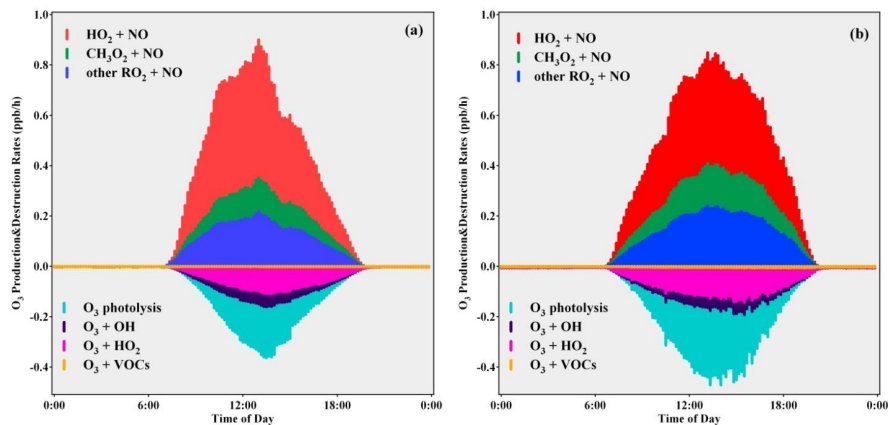


Fig. 5. Break down of O_3 in-situ production and destruction rates at WLG in (a) spring and (b) summer.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Results from the Mt.
Waliguan
Observatory

L. K. Xue et al.

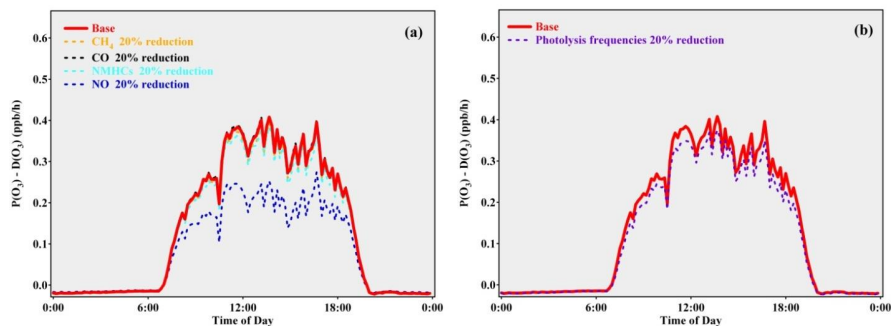


Fig. 6. Sensitivity of summertime O_3 production rates to (a) ozone precursors and (b) photolysis frequencies at WLG.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Results from the Mt.
Waliguan
Observatory

L. K. Xue et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

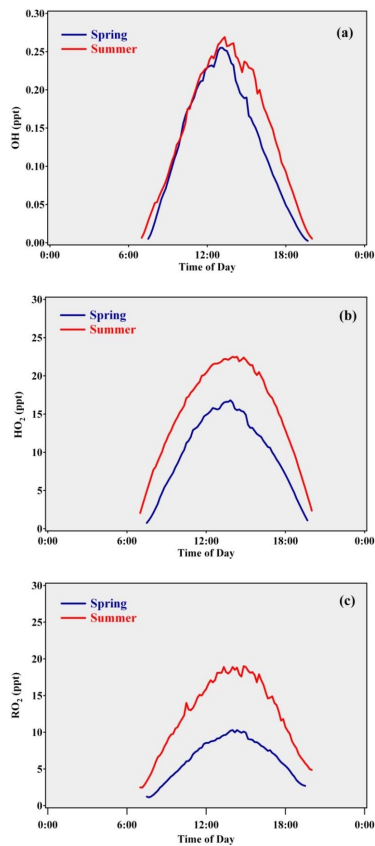


Fig. 7. Model-predicted daytime profiles of (a) OH, (b) HO₂, and (c) RO₂ at WLG.

Results from the Mt. Waliguan Observatory

L. K. Xue et al.

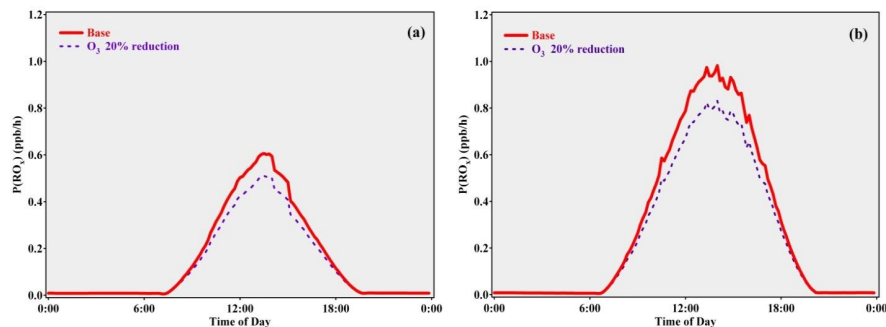


Fig. 8. Sensitivity of RO_x production rates to surface O_3 levels at WLG in **(a)** spring and **(b)** summer.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)