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Observations of high level of ozone at Qinghai Lake basin in the northeastern Qinghai-Tibetan Plateau, western China

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Abstract Measurements of surface ozone (O_3), nitrogen oxides (NO_x = NO + NO_2), carbon monoxide (CO), and dew point were made at Qinghai Lake (QHL), China, a basin in the remote Tibetan Plateau area, in October 2010 and October 2011. The O_3 mixing ratio was found to be high with average of 41±9 ppb in October 2010 and 57±10 ppb in October 2011. The observed diurnal pattern of O_3 mixing ratio was characterized by a minimum between 07:00 and 10:00 local standard time (LST) increasing ~20 ppb to a broad peak occurring

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between 13:00 and 18:00 LST. This diurnal pattern differs substantially from that observed at WMO's GAW Baseline Observatory located above the basin on Mount Waliguan, ~130 km southeast of QHL. The elevated O_3 mixing ratios observed in the afternoon are attributed to in situ photochemical production in the air trapped in the QHL basin by surrounding mountains. The low O_3 mixing ratios observed in the morning are most likely due to surface removal in a shallow nocturnal boundary layer. The data indicate substantial impacts of pollution on air quality even in this remote area. The high O_3 values observed in 2011 may cause observable damage to the vegetation, adding stress to an ecosystem ready under the threat of desertification.

Key words Ozone · Photochemical production · Qinghai-Tibetan Plateau

1 Introduction

Ozone (O_3) is a key atmospheric trace gas with climate and air quality importance (Guttikunda et al. 2005; Sitch et al. 2007; Selin et al. 2009; Cooper et al. 2012; Tie et al. 2013). Although ~90 % of O_3 molecules are in the stratosphere, the remaining 10 % of column O_3 in the troposphere plays a critical role in influencing air quality and atmospheric chemistry (Cristofanelli et al. 2010). As the precursor of highly reactive hydroxyl (OH) radicals, O_3 regulates the oxidative capacity of the atmosphere determining the lifetime of many gases (Kumar et al. 2010). Due to its high chemical reactivity, elevated surface O_3 is harmful to human health, natural ecosystems, and crop yields (Chameides et al. 1999; Mudway and Kelly 2000; Mauzerall and Wang 2001; Ashmore 2005; Ahmad et al. 2013). The budget of O_3 in the troposphere is determined by the photochemistry involving volatile organic compounds (VOCs) and nitrogen oxides (NOx), downward transport from stratosphere, and dry deposition on the earth's surface (Crutzen 1973; Stohl et al. 2003; Adon et al. 2013). Additionally, O_3 also plays an important role in the atmospheric radiation balance, particularly in the middle and upper troposphere, due to its strong ultraviolet absorption and greenhouse effect (Hassler et al. 2013; Antón et al. 2014).

The Tibetan Plateau is the highest plateau in the world (average height ~4000 m above sea level), and exerts profound thermal and dynamic influences on regional and global climate (Chen et al. 2011). However, previous studies on O_3 focused mainly on rural and urban China (e.g., Wang et al. 2006a; Jiang et al. 2012; Wang et al. 2014). Relatively limited effort has been made to understand trace gas levels in the Tibetan Plateau (e.g., Ye and Xu 2003; Tian et al. 2008; Li et al. 2009; Liu et al. 2010). Qinghai Lake (QHL: 36.32°–37.12°N, 99.38°–100.45°E), the largest lake in China, is located ~3200 m above mean sea level (AMSL) in a semi-desert basin in the northeast of the Tibetan Plateau (Fig. 1). The QHL basin has a delicate ecosystem. High pollution, especially high O_3 levels, can damage or suppress the growth of vegetation and contribute to desertification (Ashmore 2005; Ahmad et al. 2013). In the present study, we observed high O_3 concentrations at QHL in October with a clear diurnal variation that was distinctly different to that observed at the Mount Waliguan Observatory despite their close proximity. We show below that the high O_3 and distinct diurnal pattern at QHL are due to a combination of pollution, photochemistry and geography.

2 Measurements

Measurements were taken from 5 to 26 October, 2010 (O_3 and NO_x) and from 17 to 26 October, 2011 (O_3 and CO) on the rooftop (~15 m above ground level) of a sampling tower at

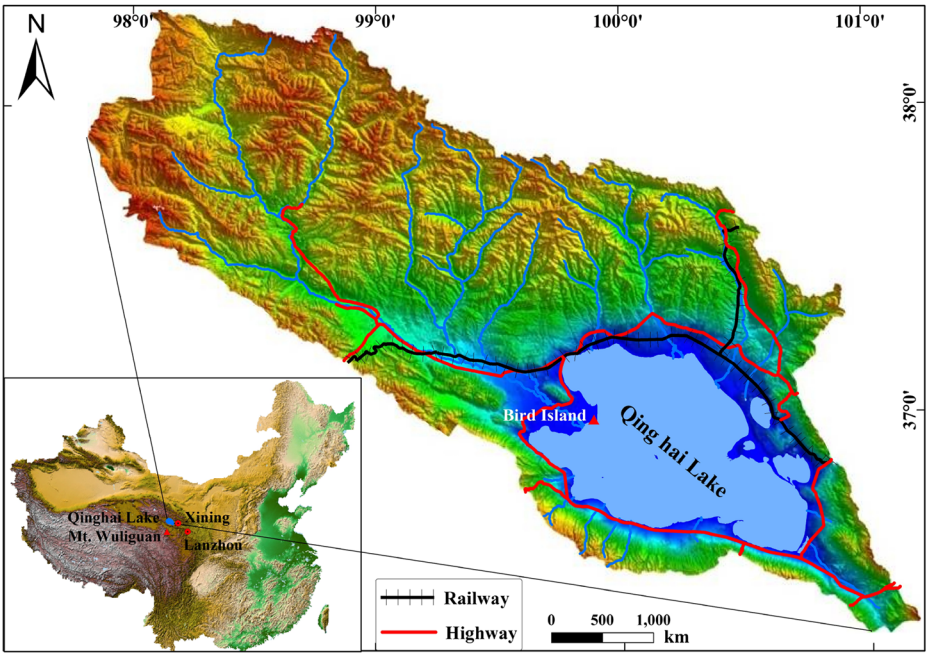

Fig. 1 The map of the sampling site at Qinghai Lake (QHL) and Mount Waliguan (WLG) as well as the surrounding regions

the "Bird Island" peninsula (36.98°N, 99.88°E, ~3200 m AMSL), which is located at the northwest section of the QHL shore as shown in Fig. 1. Five-minute average O_3 mixing ratios were recorded using an ultraviolet (UV) photometer (Ecotech Model EC9810A Ozone Analyzer, Australia) that measures O_3 in the range of 0–20,000 ppb with a detection limit of 0.5 ppb. Five-minute average NO_x was measured by a gas-phase chemiluminescence (Ecotech Model EC9841 Nitrogen Oxides Analyzer, Australia), where NO_2 is converted to NO with a molybdenum catalytic converter followed by the detection of total NO. Because the molybdenum catalytic converter may convert other nitrogen oxides in addition to NO_2 into NO, the NO_x reported here represents the upper limit of its true value. The detection limit is 0.5 ppb of NO_x. These analyzers were calibrated before the field measurements by injecting standard gases of different concentrations. Five-minute average mixing ratios of CO gas were obtained using gas-filter correlation technology with infrared photometric detection (Ecotech Model EC9830T Carbon Monoxide Analyzer, Australia) with a detection limit of 20 ppb. Hourly dew point was measured at the Gangcha national reference climatological station, ~45 km northeast from the sampling site. Surface O_3 and dew point were also measured at the Mount Waliguan Observatory (WLG: 36.28°N, 100.90°E, 3816 m AMSL), the highest GAW (Global Atmospheric Watch) station, which is located ~130 km to the southeast, and ~600 m above the basin (Fig. 1), concurrently for comparison purpose.

3 Results and discussion

The time series of O_3, NO_x and CO measured at QHL are shown in Fig. 2. For comparison, O_3 mixing ratios measured at WLG in October 2011 are also shown. The O_3 mixing ratios ranged

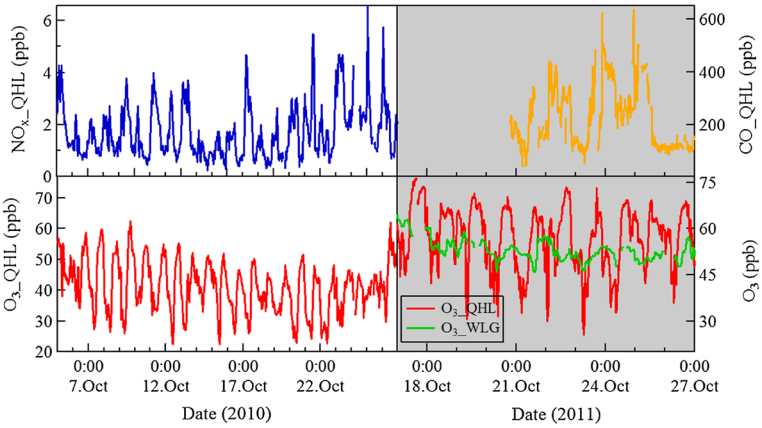

Fig. 2 Time series of 5-min averaged O_3, NOx, and CO mixing ratios at Qinghai Lake (QHL) during 2010 and 2011. The time series of O_3 mixing ratios at Mount Waliguan (WLG) during 2011 is also shown for comparison

from 22 to 62 ppb with an average of 41±9 ppb in October 2010, and from 26 to 77 ppb with an average of 57±10 ppb in October 2011. Although the absolute values show some difference, the diurnal patterns are consistent between October 2010 and October 2011, characterized by a clear diurnal pattern showing a rapid increase from daily minimum of ~23–44 ppb in the morning to daily maximum of ~62–77 ppb in the afternoon. Such large variation of O_3 mixing ratio at QHL differs significantly from what observed at WLG where the O_3 variation was only about 10 ppb. The daily minimal O_3 mixing ratio at QHL was ~25 % lower than that at WLG, while the maximal O_3 mixing ratio at QHL was ~25 % higher than that at WLG (Fig. 2). Furthermore, the diurnal O_3 variation patterns at the two sites are different as discussed below, although the distance between two sites is only ~130 km.

Figure 3 shows the diurnal patterns of the average O_3 mixing ratios and dew point for the entire measurement period at QHL and WLG, respectively. The O_3 level at WLG showed minimal value (~52 ppb) around noon local standard time (LST) and broad nocturnal maximum (~56 ppb) between 19:00 and 02:00 LST. This diurnal pattern can be explained by the following mechanism: solar radiation heats the air adjacent to the mountain slopes during the day, resulting in an anabatic wind that brings low-O_3 air from valleys below, and shortly after sunset, radiative cooling of the slopes cools the adjacent air, causing a katabatic wind that transports high-O_3 air from the free troposphere to the station. This diurnal pattern is consistent with those observed in previous studies performed in spring and summer at WLG (Wang et al. 2006b; Xue et al. 2011). Note that the average value of O_3 at WLG shown in Fig. 3b is about 53 ppb, which is ~10 ppb higher than that measured in the same month in 1996 (Zhu et al. 2004).

In contrast, the O_3 mixing ratios at QHL showed a trough between about 07:00 and 10:00 LST with a minimum value (33 ppb in 2010 and 43 ppb in 2011), followed by a sharp increase to reach daytime peak mixing ratio (49 ppb in 2010 and 67 ppb in 2011) from about 13:00 to 18:00 LST. Following the daytime peak, the O_3 mixing ratios declined continuously until the next early morning. The differences in O_3 levels and their diurnal patterns between QHL and WLG are striking although both sites are remote and not far from each other (~130 km). Compared to WLG, QHL is ~130 km further away from the highly populated cities (Xining and Lanzhou, see Fig. 1). Therefore it is unlikely that an air parcel of a high level of O_3 transported to QHL is not detected at WLG. Downward transport of stratospheric O_3 could not

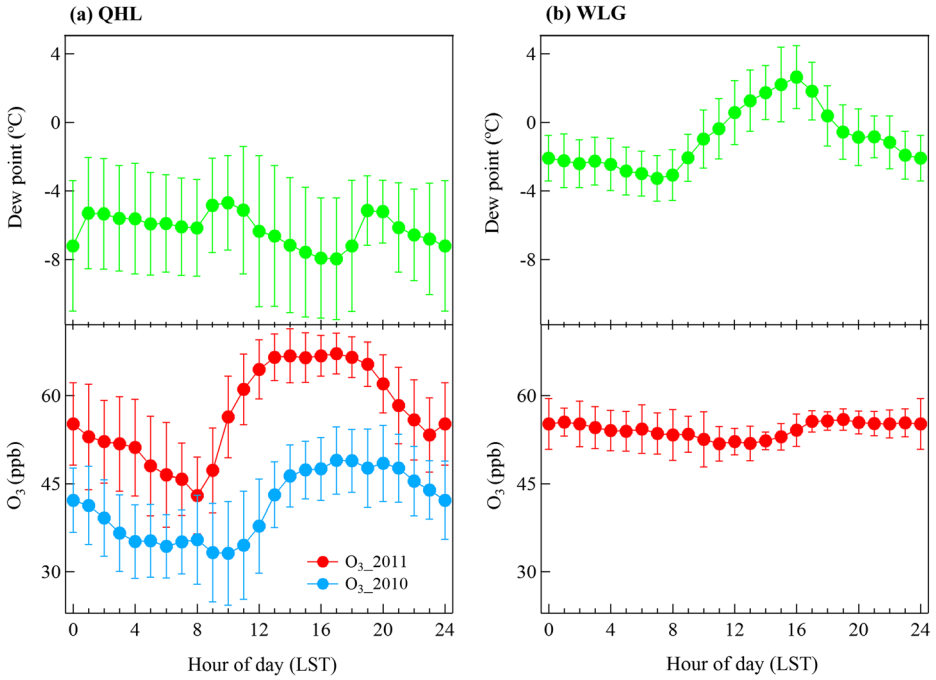

Fig. 3 Diurnal variations of O_3 mixing ratios and dew point for the entire measurement period at (**a**) Qinghai Lake (QHL) and (**b**) Mount Waliguan (WLG), respectively. *Vertical lines* indicate one standard deviation. LST stands for local standard time

explain the observed difference between these two measurement sites, either. First, WLG is about 600 m higher than QHL, and therefore expected to experience the downward transport more often and intensely. However, the daily maximum O_3 mixing ratios at WLG were around 25 % lower than those at QHL. Second, measurements of O_3 vertical profiles at Xining (the city ~180 km away from QHL) showed the concentrations < 70 ppb at the altitude below 8 km (Liu et al. 1997). Thus, downward transport of ozone rich air parcels to surface at QHL is very likely not a major contributor because there was no strong convection during the measurement periods. Figure S1 and Figure S2 of the supplementary data show that Aqua and Terra satellite images around local noon did not show significant convective clouds. Although dew point drops a few degrees in the afternoon (an indication of mixing of dry air from higher altitudes into the boundary layer, see Fig. 3), the O_3 mixing ratios at QHL reach the maximum before the downwind transport begins.

In the troposphere, O_3 is formed through photochemical reactions in the presence of O_3 precursors, including the nitrogen oxides (NO_x = NO + NO_2), carbon monoxide (CO), and volatile organic carbons (VOCs) (Kumar et al. 2013). As shown in Fig. 2, significant amount of NO_x and CO are found in the boundary layer. The NO_x and CO mixing ratios varied from 0.5 to 7 ppb and from 34 to 634 ppb, respectively. Although this region is remote, each day thousands of diesel vehicles pass through the QHL basin via national highways surrounding the lake and these vehicles are likely the main source of NO_x (and a CO source as well). Biofuel (including yak and sheep dung, firewood, and crop residues) is the main energy source in rural Qinghai, accounting for ~80 % of total household energy, of which ~65 % from burning yak and sheep dung (Ping et al. 2011). The basin also hosts a coalmine with unknown

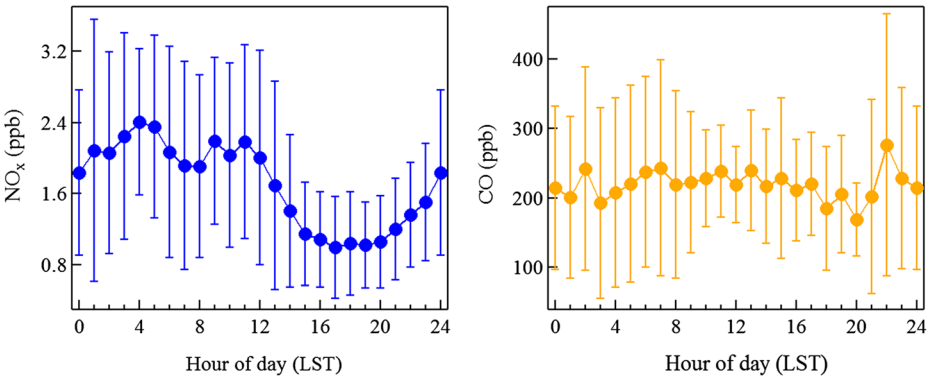

Fig. 4 Diurnal variations of NOx and CO mixing ratios at Qinghai Lake during October 2010 and 2011, respectively

power source and consumption. Trash burning is prevalent in this area. These pollution sources could contribute to significant amount of CO and VOCs as well as NO_x. The diurnal averages of NO_x and CO are shown in Fig. 4. Average daily decrease in NO_x from the morning to afternoon is about 1 ppb. This change is much smaller than the magnitude of O_3 increase (>10 ppb), indicating that the sharp daily increase of O_3 is not simply due to NO_2 photolysis.

It is likely that the high O_3 mixing ratio and its distinct diurnal pattern at QHL are consequence of a combination of geographic location, meteorological conditions, and in situ photochemistry. The large QHL basin is only aerated with fresh air at surface when the boundary layer is higher than the surrounding mountains. The dew point measurements suggest that this only happens after late morning, and only lasts until early evening. Surface air is trapped in the basin for the rest of time. After sunset, a very shallow inversion surface layer may develop (Whiteman et al. 2008; 2010). O_3 trapped in this layer may be gradually consumed by a combination of dry deposition and titration by NO, but quickly replenished in the morning as the boundary layer height grows. Throughout the daytime O_3 is produced photochemically in the basin; and may be transported to the free troposphere only when the boundary layer height is above the surrounding mountains, which is about 600–800 m above the lake. Overall, the situation encountered at QHL basin is similar to the Upper Green River Basin of Wyoming reported by Schnell et al. (2009) and Carter and Seinfeld (2012).

4 Concluding remarks

High mixing ratios of O_3 and a distinct diurnal pattern have been observed at Qinghai Lake (QHL), China. The daily O_3 concentrations varied from 26 to 77 ppb, much larger than those observed at the nearby GAW Waliguan (WLG) station. The difference in diurnal cycle of O_3 between these two locations is striking even though the distance between these two sites are only ~130 km, suggesting the combined effects from local geography, meteorology, and air pollution. The diurnal variation of QHL O_3 can be attributed to in situ photochemical production during the day and dry deposition at night. Emissions from heavy duty trucks around QHL could be an important source responsible for the high O_3 levels at the QHL region. Our results suggest that further measurements (e.g., speciated reactive nitrogen compounds and volatile organic carbons) are needed for a better understanding of O_3 pollution at the pristine Tibetan Plateau.

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