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Causes of increasing ozone and decreasing carbon monoxide in springtime at the Mt. Bachelor Observatory from 2004 to 2013

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HIGHLIGHTS

- We examined 10-year trends in springtime O_3 and CO at the Mt. Bachelor Observatory.
- Median O_3 increased by 1.7% yr^{-1} while median CO decreased by −1.9 yr^{-1}.
- HYSPLIT cluster analysis suggests the impact of ALRT on western U.S. springtime O_3.
- Reductions in Northern Hemisphere emissions likely influenced springtime CO.
- Trends suggest that North Pacific OH may have increased over the study period.

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ABSTRACT

We report trends in springtime ozone (O_3) and carbon monoxide (CO) at the Mt. Bachelor Observatory (MBO) in central Oregon, U.S.A. from 2004 to 2013. Over the 10-year period the median and 95th percentile springtime O_3 increased by 0.76 ± 0.61 ppbv yr^{-1} (1.7 ± 1.4% yr^{-1}) and 0.87 ± 0.73 ppbv yr^{-1} (1.5 ± 1.2% yr^{-1}), respectively. These trends are consistent with reported positive trends in springtime O_3 in the western U.S. In contrast, median CO decreased by −3.1 ± 2.4 ppbv yr^{-1} (−1.9 ± 1.4% yr^{-1}), which is highly similar to springtime North Pacific surface flask measurements from 2004 to 2012. While a 10-year record is relatively short to evaluate long-term variability, we incorporate transport model analysis and contextualize our measurements with reported northern mid-latitude trends over similar time frames to investigate the causes of increasing O_3 and decreasing CO at MBO. We performed cluster analysis of 10-day HYSPLIT back-trajectories from MBO and examined O_3 and CO trends within each cluster. Significant positive O_3 trends were associated with high-altitude, rapid transport from East Asia. Significant negative CO trends were most associated with transport from the North Pacific and Siberia, as well as from East Asia. The rise in springtime O_3 is likely associated with increasing O_3 precursor emissions in Asia and long-range transport to the western U.S. The decline in springtime CO appears linked to decreasing Northern Hemisphere background CO, largely due to anthropogenic emissions reductions in Europe and North America, and also to a recently reported decline in total CO output from China caused by more efficient combustion. These springtime O_3 and CO trends suggest that hydroxyl radical (OH) mixing ratios in the North Pacific may have increased over the study period.

1. Introduction

Surface ozone (O_3) is integral to tropospheric chemistry and has adverse impacts on human health and the environment (Monks et al., 2009; McDonald-Buller et al., 2011). It is a secondary pollutant produced through photochemical reactions involving naturally or anthropogenically emitted nitrogen oxides (NO_x), carbon monoxide (CO), methane (CH_4), and volatile organic compounds (VOCs) (Monks et al., 2009; Cooper and Ziemke, 2013). It is destroyed by reactions involving water vapor and photolysis and is the major source of the hydroxyl radical (OH) (Monks et al., 2009; Parrish et al., 2013). Ozone also originates in the stratosphere and can be transported to the troposphere (Langford et al., 2009; Lin et al., 2012a). The O_3 lifetime is days in the boundary layer, but weeks in the free troposphere; thus it can be transported on continental scales (Zhang et al., 2008).

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Tropospheric O_3 in northern mid-latitudes has a well-known seasonal cycle linked to photochemistry, with a summer maximum in urban areas and late spring maximum in remote areas (Parrish et al., 2013). In some locations, elevated springtime O_3 has also been attributed to stratosphere-to-troposphere transport (Langford et al., 2009). Peak O_3 concentrations have recently shifted to earlier in the year, perhaps due to changes in atmospheric transport, emissions, and/or climate change (Parrish et al., 2013). Lin et al. (2014) reported that seasonal O_3 trends in the sub-tropical North Pacific are influenced by a combination of precursor emissions and decadal-scale shifts in atmospheric circulation, demonstrating how climate variability may impact surface O_3.

Recent changes in O_3 precursor emissions have had a demonstrated impact on regional O_3 production (Cooper and Ziemke, 2013; Hartmann et al., 2013). For example, surface O_3 increased at some northern mid-latitude European locations from 1950 until the late 1990s, likely due to economic and industrial growth; however, the rate of O_3 production at those sites has since slowed or declined, whereas surface O_3 has increased in East Asia since 1990 while downwind of Asia O_3 trends are variable (Parrish et al., 2012; Cooper and Ziemke, 2013; Hartmann et al., 2013; Oltmans et al., 2013). In the U.S., NO_x emissions controls have led to significant reductions in summertime O_3 and in the frequency and magnitude of high-O_3 events at several eastern U.S. sites (Cooper et al., 2012; He et al., 2013; Rieder et al., 2013). In contrast, springtime O_3 has increased significantly in the western U.S. free troposphere and at 50% of rural surface sites, likely due to trans-Pacific transport of Asian air masses that can increase baseline free tropospheric O_3 (Cooper et al., 2012). High-O_3 events at high-elevation western U.S. sites have been linked to Asian long-range transport (ALRT) and subsidence of O_3-rich air from the upper troposphere/lower stratosphere (UT/LS) (Ambrose et al., 2011; Lin et al., 2012a, 2012b). The U.S. primary O_3 National Ambient Air Quality Standards (NAAQS) is 75 ppbv, but reduction to 60–70 ppbv has been proposed (U.S. EPA, 2010). In the western U.S., where free tropospheric air affected by inter-continental pollution transport or episodic stratospheric intrusions can significantly influence surface O_3, NAAQS compliance may be a challenge (Parrish et al., 2010; Jaffe, 2011; Lin et al., 2012a, 2012b; Wigder et al., 2013a).

Carbon monoxide (CO) is emitted to the atmosphere as a product of incomplete combustion (e.g. fossil fuel and biomass burning) and is a precursor for carbon dioxide (CO_2) and O_3, while reaction with OH is the dominant sink (Worden et al., 2013). The CO lifetime is weeks to months; thus it has been used as a tracer of long-range pollution transport to the western U.S. (Price et al., 2004; Weiss-Penzias et al., 2006). Over the past decade or more, anthropogenic CO emissions in Europe and North America have declined, while emissions from China and India have increased; however, anthropogenic emissions inventories show large discrepancies, while biomass burning emissions estimates vary both spatially and temporally (Granier et al., 2011; Tohjima et al., 2013). Yet recent declines in Northern Hemisphere CO (Novelli et al., 2003; Hartmann et al., 2013; Worden et al., 2013) may suggest the impact of regional anthropogenic emissions reductions on atmospheric CO.

Here, we present springtime O_3 and CO trends from 2004 to 2013 at the Mt. Bachelor Observatory (MBO) in central Oregon, U.S.A. The location and elevation of MBO (43.979°N, 121.687°W, 2763 m asl) and the lack of large local anthropogenic emission sources upwind are optimal for sampling free tropospheric air and ALRT (Weiss-Penzias et al., 2006; Ambrose et al., 2011; Fischer et al., 2011). The greatest influence of trans-Pacific transport on the western U.S. is observed in spring due to ventilation of the East Asian boundary layer by mid-latitude cyclones and convection, and circulation of trans-Pacific pollution plumes around the Pacific High (Liang et al., 2004; Stohl et al., 2002; Zhang et al., 2008). We acknowledge that a 10-year record is relatively short for trend analysis; however, free troposphere measurements, including ozonesonde and aircraft measurements, have varying limitations related to data frequency and sampling location, and yet these datasets all provide important insights into global trends. While the MBO observations do not allow for examining inter-decadal variability in tropospheric concentrations and atmospheric transport, we combine measurements with transport model analysis and other reported long-term trends to identify possible causes of springtime O_3 and CO trends at this western U.S. free tropospheric site over the 10-year study period.

2. Methods

2.1. Measurements at MBO

Measurements at MBO began in February 2004. Continuous measurements include a suite of chemical (e.g. O_3, CO, aerosol scattering, mercury) and meteorological (e.g. wind speed/direction, temperature, relative humidity) parameters (Ambrose et al., 2011). Non-continuous measurements (e.g. for specific seasons or studies) include compounds such as nitrogen oxides (NO_x and NO_y) and peroxy acetyl nitrate (PAN).

Ozone measurements are made using a Dasibi 1008 RS UV Photometric Ozone Analyzer (Weiss-Penzias et al., 2006; Ambrose et al., 2011). Monthly automated zeroes are performed using a charcoal scrubber cartridge. The analyzer is calibrated every six months with an O_3 generator referenced to a Washington State Department of Ecology transfer standard, which is calibrated against the EPA Region 9 Standard Reference Photometer. The method detection limit (MDL) is 1 ppbv and the estimated total uncertainty is ±2% (Ambrose et al., 2011).

Carbon monoxide was measured during spring 2004 using a Thermo Electron Corporation (TECO) 48C nondispersive infrared analyzer, and thereafter using a TECO 48C Trace Level Enhanced (TLE) analyzer (Ambrose et al., 2011) through April 2012. These analyzers were calibrated every 24 h with a ±2% NIST-traceable working standard of 400–500 ppb referenced to a NOAA-certified breathing air primary standard. Zeroes were performed every two hours. The MDL was 20 ppbv and the estimated total uncertainty in hourly-averaged mixing ratios was ±6%. Since 1-May-2012, CO has been measured using the Picarro G2302 Cavity Ring-Down Spectrometer (Chen et al., 2013). Calibrations are performed every eight hours using NOAA calibration gas standards, which are referenced to the World Meteorological Organization's (WMO) mole fraction calibration scale. The estimated MDL is 1 ppbv with estimated total uncertainty of ±3.4%.

Although CO was measured using different instruments over the study period, they were consistently calibrated using certified calibration gases. Additionally, the TECO 48C TLE and Picarro G2302 analyzers were operated concurrently with a NOAA Programmable Flask Package during 2012. The Picarro measurements compared extremely well against discrete flask measurements ($y = 0.97x + 2.4$; $r^2 = 0.97$; $n = 145$). A comparison of hourly-averaged TECO 48C TLE versus Picarro G2302 CO measurements demonstrated that the TECO was relatively noisier than the Picarro ($y = 1.06x - 13.7$; $r^2 = 0.99$; $n = 2959$). At the average springtime hourly CO mixing ratio from April 2004 to April 2012 (144 ppbv; typical of free tropospheric values), we calculated a mean bias of −5 ppbv for the TECO measurements. We applied the above equation to the TECO CO measurements from April 2004 through April 2012 to correct for this bias and used the corrected data in this manuscript. Springtime CO trends were highly similar between corrected and uncorrected data. Additional information on the CO measurement inter-comparison and springtime trends calculated