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Regional and hemispheric influences on temporal variability in baseline carbon monoxide and ozone over the Northeast US

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HIGHLIGHTS

- Decreasing low elevation baseline CO linked to anthropogenic emission reductions.
- Constant baseline CO at high elevation caused by U.S. and Asian emissions.
- Increasing coastal baseline O3 in winter-spring owing to NOx emission reductions.
- 2001-10 baseline CO/O3 shaped by Global fire/anthropogenic emissions & meteorology.

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ABSTRACT

Interannual variability in baseline carbon monoxide (CO) and ozone (O_3), defined as mixing ratios under minimal influence of recent and local emissions, was studied for seven rural sites in the Northeast US over 2001–2010. Annual baseline CO exhibited statistically significant decreasing trends (−4.3 to −2.3 ppbv yr^{-1}), while baseline O_3 did not display trends at any site. In examining the data by season, wintertime and springtime baseline CO at the two highest sites (1.5 km and 2 km asl) did not experience significant trends. Decadal increasing trends (~2.55 ppbv yr^{-1}) were found in springtime and wintertime baseline O_3 in southern New Hampshire, which was associated with anthropogenic NO_x emission reductions from the urban corridor. Biomass burning emissions impacted summertime baseline CO with ~38% variability from wildfire emissions in Russia and ~22% from Canada at five sites and impacted baseline O_3 at the two high elevation sites only with ~27% variability from wildfires in both Russia and Canada. The Arctic Oscillation was negatively correlated with summertime baseline O_3, while the North Atlantic Oscillation was positively correlated with springtime baseline O_3. This study suggested that anthropogenic and biomass burning emissions, and meteorological conditions were important factors working together to determine baseline O_3 and CO in the Northeast U.S. during the 2000s.

1. Introduction

Carbon monoxide (CO) is a product of incomplete combustion (e.g. fossil fuel, biofuel, and biomass burning) and oxidation of hydrocarbon compounds (Worden et al., 2013). In the presence of nitrogen oxides (NO_x), oxidation of volatile organic compounds (VOCs) and CO can lead to the photochemical formation of ozone (O_3). CO is a major sink of hydroxyl radicals (OH) and O_3 is a precursor of OH, and hence they significantly affect the oxidizing capacity of the troposphere (Prinn, 2003). Tropospheric CO and O_3 are also serious and ubiquitous air pollutants, affecting human and natural ecosystem's health (EPA, 2012).

CO has been used as a tracer of anthropogenic influence and fire emissions, due to its relatively unreactive chemical nature (Gratz et al., 2014; Price et al., 2004). A positive correlation between CO and O_3 has been identified in summer at various locations, attributed largely to the predominant influence of photochemical processes (Mao and Talbot, 2004; Hegarty et al., 2009). Therefore, many studies have used O_3-CO correlation to constrain O_3 sources and transport (e.g., Mao and Talbot, 2004; Hudman et al., 2009; Kim

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et al., 2013). The O_3-CO relationship was more complicated in other seasons due to the effects of stratospheric intrusion, dry deposition of O_3, or titration of O_3 by NO (Mao and Talbot, 2004; Voulgarakis et al., 2011; Kim et al., 2013).

The United States has made enormous efforts to control ambient mixing ratios of criteria pollutants since the 1970s (EPA, 2012). Nationally, annual second maximum 8 h average mixing ratios of CO decreased by 52%, and annual mean mixing ratios of nitrogen dioxide (NO_2) declined by 33% over 2001–2010 (EPA, 2012). Although anthropogenic emissions have decreased in Europe and North America, emissions in China and India have increased. Biomass burning emissions vary both spatially and temporally (Granier et al., 2011). The lifetime of CO and O_3 in the free troposphere is ~2 months and ~20 days, respectively (Price et al., 2004; Stevenson et al., 2006). Thus, transport of CO, other O_3 precursors, and O_3 from an upwind region as well as amounts produced in transit could affect downwind baseline CO and O_3 levels (Oltmans et al., 2008; Pollack et al., 2013). It remains unclear how opposing changes in emissions over North America, Europe and Asia have globally affected baseline CO and O_3, which are defined as mixing ratios of CO and O_3 under minimal influence of recent and local emissions (Chan and Vet, 2010; HTAP, 2010).

The terms “background” and “baseline” have often been used interchangeably, and a few studies discussed the difference (HTAP, 2010; Huang et al., 2015). The term “background” was used in modeling studies that estimated the atmospheric mixing ratio of a compound determined by natural sources only, while the term “baseline” was obtained from measurement records by removing data affected by local influences (Chan and Vet, 2010). Various methods have been utilized to diagnose baseline conditions, including using measurements at remote sites, analysis of the probability distribution of pollutants, correlations with reactive nitrogen oxides, or isentropic back-trajectories (e.g., Lin et al., 2000; Derwent et al., 2007; Wilson et al., 2012). Air masses with monthly to annual low percentile values of CO are commonly considered baseline air (e.g., Lin et al., 2000; Mao and Talbot, 2012). The monthly 10th percentile value of afternoon CO was defined as baseline CO in this study for the lower elevation sites while the monthly 50^{th} percentile value of afternoon CO was used at high elevation sites. Baseline O_3 was then estimated as the monthly median of the afternoon O_3 data corresponding to CO mixing ratios below the baseline CO level (Lin et al., 2000). It should be noted that the monthly baseline CO and O_3 defined here excluded the influence of processes on hourly to daily time scales (DeBell et al., 2004; Honrath et al., 2004; Dutkiewicz et al., 2011b).

Trends in baseline O_3 have been investigated for northern hemispheric mid-latitude regions, such as North America, Europe, and Asia, and no consistent trends have been found (e.g., Chan, 2009; Cui et al., 2011; Logan et al., 2012; Oltmans et al., 2013; Wilson et al., 2012; Cooper et al., 2010; Xu et al., 2008). However, decreasing trends were found in baseline CO and CO concentrations in rural areas since the end of the 1980s (e.g., Hallock-Waters et al., 1999; Novelli et al., 2003; Duncan and Logan, 2008). Interpretation of long-term trends is difficult because interannual variability in emissions, climate, and photochemistry are intricately interwoven (Hess and Lamarque, 2007). CO is a long-lived tracer of combustion and using changes in CO, one can estimate continental influences on O_3 globally (Hudman et al., 2009). However, only a few studies (Kumar et al., 2013; Gratz et al., 2014) investigated the long-term trends in baseline CO and O_3 together. Kumar et al. (2013) found that trends of −0.31 and −0.21 ppbv yr^{-1} for CO and O_3, respectively, at the Pico Mountain Observatory could be attributed to the North American anthropogenic emission declines over 2001–2010, and that climate change may have affected the intercontinental transport of O_3. Gratz et al. (2014) found that the springtime median mixing ratio of O_3 increased at a rate of 0.76 ppbv yr^{-1} at the Mt. Bachelor Observatory over 2004–2013, while median CO decreased at a rate of −3.1 ppbv yr^{-1}. Overall, causes for temporal variability in both baseline O_3 and CO have not been adequately explained.

Although a number of studies have been conducted to understand the distributions of surface CO and O_3 in the Northeast US and their controlling mechanisms (e.g. Bae et al., 2011; DeBell et al., 2004; Mao and Talbot, 2004; Schwab et al., 2009), little work has been done on baseline CO and O_3 together using long-term measurement data for the region, in particular using the data from the seven sites in this study. Here, we aimed to examine the trends in baseline CO and O_3 as well as interannual and seasonal variation at seven rural sites in the Northeast U.S. over 2001–2010 and investigate their potential association with emissions, dynamics, and O_3 photochemistry.

2. Methods and data

2.1. Measurement data

Our study used long-term observations at seven rural sites in the Northeast US. Five are located in rural New Hampshire (NH) and two are in rural New York (NY) State. These sites are 100–200 km away from major sources (Table 1 and Fig. 1). The Appledore Island (AI) site is located in the marine boundary layer, ~11 km offshore in the Gulf of Maine, while the Thompson Farm (TF) site is located in an open lot surrounded by agricultural fields and mixed vegetation, ~21 km away from the coastline. The Castle Spring (CS) and Pack Monadnock (PM) sites are ~75 km to the northwest and west of TF, respectively. These four sites are on the eastside of the Appalachian Mountain Range. The Mountain Washington Observatory (MWO) and Whiteface Mountain (WFM) sites are located on the summit of the Appalachians, ~2 km and 1.5 km a.s.l., respectively. The Pinnacle

Table 1
Ground stations with geographical coordinates and measurement periods.

Site	Latitude	Longitude	Elevation	Measurement Period (CO)	Measurement Period (O_3)	Time Resolution (min)
Appledore Island (AI)[a]	42.97°N	70.62°W	18 m	Jul, 2001–Jul, 2011	Jul, 2002–Mar, 2012	1
Thompson Farm (TF)	43.11°N	70.95°W	23 m	Apr, 2001–Jul, 2011	Apr, 2001–Aug, 2010	1
Mt. Washington (MWO)	44.27°N	71.30°W	1917m	Apr, 2001–Apr, 2009	Apr, 2001–May, 2010	1
Castle Spring (CS)	43.75°N	71.35°W	396 m	Apr, 2001–Jun, 2008	Apr, 2001–May, 2008	1
Pack Monadnock (PM)	42.86°N	71.88°W	698 m	Jun, 2004–Jul, 2011	Jul, 2004–Oct, 2008	1
Whiteface Mountain (WFM)	44.40°N	73.90°W	1484 m	Jan, 1996–Dec, 2010	Jan, 1996–Dec, 2010	60
Pinnacle State Park (PSP)	42.09°N	77.21°W	504 m	Jan, 1997–Dec, 2010	Jan, 1997–Dec, 2010	60

Note: The time in all of the datasets was expressed in coordinated universal time (UTC), i.e. local time +5 h for non-daylight saving time and +4 h for daylight saving time (March–November).

[a] CO at AI was measured seasonally from May to September over 2001–2006 and year-round over 2007–2011, and O_3 was measured seasonally from May to September over 2002–2007 and year-round over 2008–2011.