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Estimates of background surface ozone concentrations in the United States based on model-derived source apportionment

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HIGHLIGHTS

- We present a new approach for characterizing background O_3.
- Highest background occurs during the spring and tends to be related to STT-S.
- Background contributes significantly to total O_3 during non-summer months.
- At urban sites background contributes significantly to mid-range concentrations.

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ABSTRACT

We analyze background surface ozone (O_3) concentrations as estimated by coupled GEOS-Chem/CAMx models for 23 monitoring sites across the US at high- and low-elevation, rural and urban locations during 2006. Specifically, we consider hourly contributions from global tropospheric O_3 entering North America, stratospheric O_3 over North America, and natural O_3 formed from continental biogenic, fire, and lightning sources according to CAMx source apportionment calculations. Unlike historical modeled background definitions that reflect the absence of anthropogenic emissions, we define "Emissions-Influenced Background" (EIB), which includes chemical interactions with anthropogenic emissions and thus reflects "current" background levels at the sites analyzed. We further define global background O_3 (GBO_3) as the sum of the global tropospheric and stratospheric components and find that higher modeled GBO_3 occurs during the spring at sites across the US. At many of the sites during the spring, fall, and winter months higher GBO_3 is associated with more frequent stratosphere-to-troposphere transport to the surface (STT-S) events according to independent three-dimensional trajectories based on global meteorological analyses. Patterns of higher spring EIB O_3 are followed by lower values during the summer, due to heightened chemical interaction with anthropogenic sources, which are then followed by rising EIB O_3 during the fall and winter months. For some high-elevation western US sites, this seasonal pattern is less discernible due to relatively small anthropogenic contributions and the high EIB O_3 estimated throughout the year. EIB O_3 at all high-elevation sites contributes a significant proportion to total O_3 throughout the year and throughout the observed total O_3 frequency distribution, while EIB O_3 at most urban sites contributes a major portion to total O_3 during non-summer months and to the mid-range concentrations (30–50 ppb) of the frequency distribution.

1. Introduction

While background ozone (O_3) cannot be measured directly, estimating it accurately is important. Background approximations directly affect estimated human health risk and policy expectations regarding emission reduction effectiveness. McDonald-Buller et al.

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(2011) and the US Environmental Protection Agency (EPA, 2013) provide a summary of the concepts associated with background O_3 and its relevance to US air quality. Prior to 2006, O_3 measurements from remote monitoring sites were used to estimate background. EPA (1996) estimated hourly average summer background concentrations of 30–50 ppb and applied a background of 40 ppb in its risk analyses. EPA (2006) cited the work of Fiore et al. (2002, 2003), who applied the GEOS-Chem global model to estimate a mean background concentration range of 15–35 ppb. At that time, EPA (2006) defined North American background (NAB) O_3 to include contributions from global anthropogenic and natural sources in the absence of North American (i.e., U.S., Canada, Mexico) anthropogenic emissions. More recently, EPA (2013) has defined US background (USB) O_3 concentrations to include anthropogenic contributions from Canada and Mexico. Modeling results reported by EPA (2013) indicate USB and NAB concentrations tend to be higher in the West (particularly in the Intermountain West) and in the Southwest compared to the East in both spring and summer.

Background O_3 over North America has been recently estimated using the GEOS-Chem global model (Wang et al., 2009; Zhang et al., 2011), the EPA Community Multi-scale Air Quality (CMAQ) regional model (Mueller and Mallard, 2011), the regional Comprehensive Air quality Model with extensions (CAMx; Emery et al., 2012), and the AM3 global model (Lin et al., 2012). Each of these efforts have reported incremental improvements, especially for the higher concentration ranges, by using greater resolution, updated modeling systems, and improved emissions and meteorological datasets. The latest modeling results (Zhang et al., 2011; Emery et al., 2012; Lin et al., 2012) estimate background O_3 ranges of 25–50 ppb across the US, with the highest peaks reaching well over 60 ppb in areas affected by stratospheric intrusion and wildfires in the elevated areas of the western US. For the western US, results from Lin et al. (2012) illustrated the relative importance of stratospheric contributions to NAB.

Recent literature suggests that the stratosphere is a potentially important contributor to background O_3 at high- and low-elevation US monitoring sites (Ambrose et al., 2011; Cooper et al., 2011; Lefohn et al., 2011, 2012; Emery et al., 2012; Langford et al., 2012; Lin et al., 2012). Ambrose et al. (2011) reported that STE and long-range transport affects lower tropospheric O_3 concentrations at the Mt. Bachelor Observatory (2763 m) in central Oregon. Cooper et al. (2011) indicated that descending stratospheric intrusions and Asian pollution plumes influence O_3 concentrations along the California coast. Using trajectory analyses, Lefohn et al. (2011, 2012) reported that stratosphere-to-troposphere transport to the surface (STT-S) frequently coincides with "enhanced" surface O_3 concentrations ($\geq$50 ppb) at both high- and low-elevation monitoring sites across the US during specific months. While STT-S coincidences occur most frequently at high-elevation sites in the western and eastern US during spring, they also noted that coincidences occur at times during the summer, fall, and late winter. Applying the AM3 global chemical transport model, Lin et al. (2012) noted that STT-S during the spring and early summer contributes to surface O_3 concentrations over the western US. Previous literature over the years complement the most recent results cited above concerning the influences of the stratosphere on lower-tropospheric O_3 concentrations (e.g., Reed, 1955; Junge, 1962; Danielsen, 1968; Danielsen, 1975; Danielsen and Mohnen, 1977; Ludwig et al., 1977; Shapiro, 1980; Haagenson et al., 1981; Davies and Schuepbach, 1994; Lamarque and Hess, 1994; Schuepbach et al., 1999; Stohl et al., 2000; Lefohn et al., 2001; Cooper et al., 2005; Cristofanelli et al., 2006; Hocking et al., 2007; Ordóñez et al., 2007; Oltmans et al., 2008; Langford et al., 2009; Akriditis et al., 2010; Cristofanelli et al., 2010).

The purpose of this study is to estimate the hourly or daily background O_3 contributions to total O_3 throughout 2006 at 16 urban and 7 rural monitoring sites across the US and to explore reasons for the range of uncertainties associated with these estimates. Coupled global (GEOS-Chem) and regional (CAMx) photochemical transport modeling (Emery et al., 2012) is used to estimate 2006 global tropospheric, stratospheric, and North American natural contributions to hourly background O_3 concentrations over the US. STT-S estimates derived from Lagrangian Analysis Tool (LAGRANTO) trajectory calculations (Lefohn et al., 2012) are used to investigate relationships between simulated background contributions and observed O_3, and to characterize the seasons and locations where stratospheric and upper tropospheric O_3 contributes to elevated surface O_3 at 23 monitoring locations.

Uniquely, this study defines a new metric that we refer to as "Emissions-Influenced Background" (EIB) O_3. EIB is apportioned to global tropospheric O_3 and stratospheric O_3 entering North America (collectively referred to as Global Background O_3 or GBO_3) and natural O_3, formed in North America from continental biogenic, fire, and lightning sources. The simulation of all three EIB components includes chemical decay via interactions with North American anthropogenic and natural precursor emissions of nitrogen oxides (NO_x), volatile organic compounds (VOC), and carbon monoxide (CO). Unlike historical modeled background definitions that reflect the absence of anthropogenic emissions (thus maximizing O_3 lifetime), we define EIB to include chemical interactions with anthropogenic emissions; thus reducing O_3 lifetime in the polluted boundary layer and reflecting "current" background levels at the sites analyzed. In pristine areas with small anthropogenic influences, EIB is similar to NAB. In urban areas EIB is chemically decayed but it converges upward toward the higher NAB metric as anthropogenic emissions are reduced.

EIB O_3 estimates are subject to systematic and unsystematic model errors that vary site-to-site. Our methodology estimates the hourly range of EIB uncertainty associated with site-specific error in total O_3 by distributing that error to global and natural/anthropogenic components. The upper uncertainty range serves as a lower bound estimate for USB. Monthly and seasonal patterns of STT-S frequency are used to explore possible reasons for some of these uncertainties.

2. Approach

2.1. Selection of surface ozone monitoring sites

Measured hourly 2006 O_3 data at 23 US monitoring sites were downloaded from the EPA Air Quality System (AQS) and Clean Air Status and Trends Network (CASTNet). The 23 monitoring sites represent high/low elevation, urban/rural environments, and east/central/west geography across the US (Fig. 1; Table 1). Sixteen urban monitoring sites were analyzed in this study, one from each city addressed in the EPA's human health risk analyses (US EPA, 2012). Usually, the selected site reported the highest 3-year average of the 4th highest daily maximum 8-h average concentration over 2006–2008 (consistent with the US O_3 standard). In some cases we selected a site reporting a similar peak but more representative of the city-wide population distribution. The remaining 7 sites were singularly located in rural environments and had been previously characterized by Lefohn et al. (2012). All rural and most urban sites collected data over a 12-month period although seven of the urban sites had shorter monitoring seasons (Table 1). The 2006 data capture averaged 95% over the 23 sites.