Atmospheric Environment 88 (2014) 192–200

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

# Ozone in the southeastern United States: An observation-based model using measurements from the SEARCH network

C.L. Blanchard [a,*], G.M. Hidy [b], S. Tanenbaum [a]

[a] Envair, 526 Cornell Avenue, Albany, CA 94706, USA
[b] Envair/Aerochem, 6 Evergreen Dr, Placitas, NM 87043, USA

## HIGHLIGHTS

- Observed ozone response to weather and ozone precursors is modeled.
- Ozone responses to changing concentrations of ozone precursors are projected.
- Empirically-determined results may be compared to photochemical model predictions.
- Model is useful for relating ozone trends to precursor trends and weather.

## ARTICLE INFO

*Article history:*
Received 28 August 2013
Received in revised form
28 January 2014
Accepted 6 February 2014
Available online 7 February 2014

*Keywords:*
Ozone
SEARCH
Meteorology
$NO_x$
VOC
Generalized additive model

## ABSTRACT

A generalized additive model (GAM) is used to examine the influence of meteorological factors, nitrogen oxides ($NO_x = NO + NO_2$), and non-methane hydrocarbons (NMOC) on daily peak 8-h ozone ($O_3$) concentrations. Application to 2002–2011 monitoring data from the Southeastern Aerosol Research and Characterization (SEARCH) program showed sensitivity of peak 8-h $O_3$ to morning concentrations of nitric oxide (NO) and nitrogen dioxide ($NO_2$) and to afternoon concentrations of $NO_2$ reaction products ($NO_z$). Peak $O_3$ decreased with increasing NO and increased with increasing $NO_2$ concentrations, consistent with reactions involving $O_3$, NO, and $NO_2$. Ozone production efficiency (OPE), estimated from the modeled relation between peak 8-h $O_3$ and afternoon $NO_z$, was ~40–100 percent higher at rural compared to urban sites. OPE was nonlinear at all sites, decreasing with increasing $NO_z$ concentration. The mean ratio of $NO_z/NO_y$ showed a two-fold increase from urban to rural sites, associated with chemical aging in stagnant air masses from one day (urban sites) to two or more days (non-urban sites). Peak 8-h $O_3$ concentrations in Atlanta were sensitive to concentrations of both non-biogenic NMOC and $NO_z$. Non-urban Yorkville, Georgia, peak 8-h $O_3$ concentrations were sensitive to $NO_z$ but not to non-biogenic NMOC concentrations. The results are consistent with expected NMOC and $NO_x$ sensitivity in urban and non-urban locales.



## 1. Introduction

Ozone ($O_3$) formation is a nonlinear function of sunlight acting on ambient volatile organic compounds (VOC) and oxides of nitrogen ($NO_x$, $NO + NO_2$). Tropospheric $O_3$ mixing ratios (concentrations) are affected by solar intensity, the rate of $O_3$ formation, the rate of dispersion of $O_3$ and its precursors, meteorological factors, and transport of urban plumes.

Since 1970, emission control programs have reduced emissions and ambient concentrations of $NO_x$ and VOC, resulting in declining $O_3$ concentrations in all major metropolitan areas of the U.S. However, slow rates of $O_3$ reduction have led to concern about the reliability of predictive tools and the fundamental understanding of $O_3$ formation (e.g., National Research Council, 1991; Hidy et al., 2011).

Photochemical Air Quality Simulation Models (PAQSMs) have been used for over forty years to estimate the influence of precursor emissions on $O_3$. Complementary, observation-based modeling developed by the 1990s (e.g, NARSTO, 2000; Hidy, 2000) and is accepted by the U.S. Environmental Protection Agency (EPA) and state agencies for use in "weight-of-evidence" plans to achieve the National Ambient Air Quality Standard (NAAQS) and state standards for $O_3$ (EPA, 2007).

* Corresponding author.
*E-mail address:* cbenvair@pacbell.net (C.L. Blanchard).

http://dx.doi.org/10.1016/j.atmosenv.2014.02.006
1352-2310/

Observational and PAQSM studies suggest that $NO_x$ is the limiting $O_3$ precursor throughout much of the non-urban eastern United States (Liu et al., 1987; Sillman et al., 1990; Trainer et al., 1993; Chameides and Cowling, 1995). In the southeastern U.S., biogenic emissions of isoprene and anthropogenic $NO_x$ emissions affect $O_3$ (e.g., Chameides et al., 1988). Evidence indicates responsiveness of post-1990s $O_3$ formation to changes in $NO_x$ emissions from electric generating units (EGUs) in the eastern U.S. (Gego et al., 2007, 2008; Gilliland et al., 2008; Godowitch et al., 2008). Beginning in 1995, EPA's acid rain program (CAAA, Title IV) implemented a nationwide reduction of $SO_2$ and $NO_x$ emissions from EGUs (EPA, 2011a). The 2004 $NO_x$ state implementation plan (SIP) Call required further reductions in EGU $NO_x$ emissions in twenty-one eastern states (EPA, 2012). The Clean Air Interstate Transport Rule required 70 percent reductions of EGU emissions of $SO_2$ and $NO_x$ in 28 eastern states (EPA, 2011b).

The monitoring record from the Southeastern Aerosol Research and Characterization (SEARCH) network offers a rich data set for investigating the response of $O_3$ to emission changes. Between 1999 and 2010, the annual $O_3$-season (March–October) 95th percentiles of the peak daily 8-h $O_3$ concentrations declined at SEARCH sites by $1.1 \pm 0.4$ to $2.4 \pm 0.6$ ppbv per year (Blanchard et al., 2013a). $O_3$ declines were not attributable to a specific precursor using simple trend analyses (Blanchard et al., 2013a). Previous work suggests that the highest peak 8-h $O_3$ concentrations in Atlanta, Georgia are sensitive to both ambient NMOC and $NO_y$ ($NO_x$ plus other oxidized nitrogen species, including, e.g., $HNO_3$), but meteorological factors have a larger effect on day-to-day $O_3$ variations (Blanchard et al., 2010a).

In this paper, we use a generalized additive statistical model (GAM) to relate daily peak 8-h $O_3$ concentrations to weather, to ambient concentrations of $O_3$ precursors (NO and $NO_2$), and to $NO_x$ reaction products ($NO_z$) at SEARCH sites from 2002 to 2011. The approach is applicable to any well-instrumented monitoring location.

## 2. Methods

### 2.1. Ambient air quality measurements

Hourly measurements of gases (CO, $SO_2$, NO, $NO_2$, $NO_y$, $HNO_3$, $O_3$, and $NH_3$) were obtained from SEARCH public archives (Atmospheric Research and Analysis, 2013). Network operations and measurement methods are documented in Hansen et al. (2003, 2006), Edgerton et al. (2005, 2006; 2007; 2009), and Saylor et al. (2010). Eight sites are located in the southeastern U.S.: Pensacola, Florida (PNS) and Gulfport, Mississippi (GFP), urban coastal sites (~5 km and 1.5 km from the shoreline, respectively); Pensacola – outlying (aircraft) landing field (OLF) and Oak Grove, Mississippi (OAK), non-urban coastal sites near the Gulf (~20 km and 80 km inland, respectively); Atlanta, Georgia–Jefferson Street (JST) and North Birmingham, Alabama (BHM), urban inland sites; and Yorkville, Georgia (YRK) and Centreville, Alabama (CTR), non-urban inland sites. All sites measure meteorological parameters and gases at 10 m height (Hansen et al., 2003; Edgerton et al., 2007; Saylor et al., 2010). Measurements of NMOC, a VOC subset, were made with 24-h canister samples collected every day at JST through 2008 (Blanchard et al., 2010b). Additional 24-h and hourly NMOC measurements were made at Photochemical Assessment Monitoring Stations (PAMS) located at YRK and other sites in the Atlanta area (Blanchard et al., 2010b). Spatial and temporal variations of SEARCH air pollutant concentrations from 1999 to 2010 are described in Blanchard et al. (2013a, 2013b).

We used data from 2002 through 2011, because measurements of $NO_2$ began in 2002. Daily averages were created from hourly data. In addition, daily peak 1-h and peak 8-h NO, $NO_2$, and $O_3$ concentrations were determined for each site and day. Morning (sample start hours of 7 through 10 a.m., i.e., sampling interval of 7–11 a.m.) and afternoon (sample start hours of 12 noon through 3 p.m., i.e., sampling interval of 12–4 p.m.) concentrations of NO, $NO_2$, $NO_y$, and $NO_z$ ($NO_z = NO_y - NO - NO_2$) were also computed. Table 1 lists mean NO, $NO_2$, $NO_y$, and $NO_z$ concentrations.

### 2.2. Statistical model

EPA developed a GAM that predicts the highest daily peak 8-h $O_3$ within a metropolitan area as a function of surface and upper-air meteorological variables (Camalier et al., 2007). The EPA model (EPA, 2009) runs under the open-source R software system (The R Project, 2009). Blanchard et al. (2010a) describe an adaptation of the EPA statistical model. Further adaptation is implemented here. The GAM is expressed as:

$$\begin{aligned} l(O_3)_i = {} & \mu + f_1(x_1)_i + \ldots + f_m(x_m)_i + g_1(y_1)_i + \ldots + g_n(y_n)_i \\ & + h_1(z_1) + \ldots + h_p(z_p) + e_i \end{aligned} \quad (1)$$

Following Camalier et al. (2007), $l(O_3)_i$ is the logarithm of the peak 8-h $O_3$ on day "$i$," but either a different $O_3$ metric or a function other than the logarithm could be used. We apply the model site by site. For convenience, the terms $f_1(x_1)_i$ through $f_m(x_m)_i$ represent the effects of meteorological variables on peak 8-h $O_3$, and $g_1(y_1)_i$ through $g_n(y_n)_i$ represent the effects of ambient concentrations of $O_3$ precursors on $O_3$. For consistency with $l(O_3)_i$, the variables $y_1$ through $y_n$ are logarithms of air quality measurements. The terms $h_1(z_1)$ through $h_p(z_p)$ represent the effects of temporal variables, including "day of week" and "year". The last term, $e_i$, is the difference between observed and predicted $O_3$ (error). Each term expresses the effect of one parameter on daily peak 8-h $O_3$ as a deviation from the long-term mean, "$\mu$" (logarithm of peak 8-h $O_3$ averaged overall days). "Day of week" and "year" are categorical variables and are used to represent weekly cycles and trend, respectively. Trend need not be linear or monotonic. The GAM uses natural splines (Hastie and Tibshirani, 1990) to model nonlinear dependence of $O_3$ on other predictor variables.

Meteorological and air quality data were used to predict daily peak 8-h $O_3$ at each SEARCH site during March through October of 2002 through 2011. Camalier et al. (2007) found that the most consistently significant predictors of peak 8-h $O_3$ concentrations in the 39 eastern U.S. metropolitan areas studied were: (1) daily maximum surface temperature (T), (2) mid-day (10 a.m.–4 p.m.) relative humidity (RH), (3) morning (7 a.m.–10 a.m.) average wind speed, (4) afternoon (1 p.m.–4 p.m.) average wind speed, (5) morning (~1200 UTC) difference between 925 mb T and surface T, (6) deviation of morning (~1200 UTC) 850 mb T from 10-year monthly average, (7) air mass transport direction and distance (determined from back trajectories), (8) occurrence of rain (as number of hours), (9) julian day, (10) day of week, and (11) year. We replaced the 925 mb – surface T difference with the 850 mb T – daily minimum surface temperature because the 925 mb height in coastal areas is not always above the marine layer and may not represent temperatures aloft. We eliminated precipitation amount (or hours) and 850 mb T because they were not statistically significant at any site. We added sea-level pressure gradients from Birmingham to Mobile, AL, and from Birmingham to Atlanta.

We refit the GAM using the preceding meteorological parameters, but added the daily maximum 1-h NO and the morning $NO_2$ concentrations. The maximum NO concentrations tended to occur in the morning (hours 5 through 9 on 46–73 percent of the days), coinciding with morning traffic, while maximum $NO_2$