High ozone concentrations on hot days: The role of electric power demand and NO_x emissions

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Abstract

High ambient temperatures intensify photochemical production of tropospheric ozone, leading to concerns that global warming may exacerbate smog episodes. This widely observed phenomenon has been termed the climate penalty factor (CPF). A variety of meteorological and photochemical processes have been suggested to explain why surface ozone increases on hot days. Here, we quantify an anthropogenic factor previously overlooked: the rise of ozone precursor emissions on

hot summer days due to high electricity demand. Between 1997 and 2011, power plant emissions of NO_x in the eastern U.S. increased by ~2.5-4.0%/°C, raising surface NO_x concentrations by 0.10-0.25 ppb/°C. Given an ozone production efficiency (OPE) of ~8 mol/mol based on the 2011 NASA DISCOVER-AQ campaign, at least 1/3 of the CPF observed in the eastern U.S. can be attributed to the temperature dependence of NO_x emissions. This finding suggests that controlling emissions associated with electricity generation on hot days can mitigate the CPF.

1. Introduction

Global mean temperature has increased about 0.8°C since the late 19th century, and is projected to increase another 0.4°C over the next two decades [*IPCC*, 2007]. Temperature is one of the most important factors influencing the abundance of ozone (O_3) near the surface [*EPA*, 2006]. Greater ozone pollution associated with more prevalent heat waves is a clear adverse effect of climate change [*EPA*, 2006]. Previous studies (summarized in *Jacob and Winner* [2009]) project an increase of 1 to 10 parts per billion by volume (ppbv) in ground level ozone due to climate change over the next several decades.

The CPF, defined as $\frac{\partial[O_3]}{\partial T}$, has been used to quantify the effect of climate change on ozone pollution. *Bloomer et al.* [2009] quantified CPF in the eastern U.S. to be ~3.2 ppbv/°C prior to 2002 and ~2.2 ppbv/°C after 2002, based on analysis of ground level ozone and temperature measurements at rural sites. Surface ozone levels in the eastern U.S. have steadily declined during the past decade due to reductions in the

45 emission of NO_x from power plants following the EPA NO_x state Implementation
46 Plan (SIP) as well as reduced vehicular emissions of NO_x [e.g., *Bloomer et al.*, 2009;
47 *Cooper et al.*, 2012]. The photochemical production of tropospheric ozone in the
48 eastern U.S. is controlled by NO_x [e.g., *Sillman*, 1999]. *Bloomer et al.* [2009] related
49 the decline in the CPF after 2002 to reductions in emissions of NO_x from power
50 plants.

51 Several possible explanations for the positive value of the CPF (i.e., the rise in
52 surface ozone with increasing temperature) have been suggested. These include
53 enhanced thermal decomposition of peroxyacyl nitrate (PAN) and increased
54 anthropogenic and biogenic emissions of volatile organic compounds (VOCs) as the
55 lower atmosphere warms, as well as the correlation of subsidence, wind stagnation,
56 and UV radiation (increasing photolysis rates) with the meteorological conditions
57 associated with high temperature [*Mickley et al.*, 2004; *EPA*, 2006]. Anthropogenic
58 emissions of NO_x can also vary with temperature. Hot summer days are often
59 associated with increased emissions of NO_x from power plants to meet greater
60 electricity demand for air conditioning. *Singh and Sloan* [2005] reported that
61 vehicular emissions of NO_x increase slightly, about 1%/°C, between 20 and 35°C.
62 Auxiliary electricity generators such as backup diesel generators at hospitals running
63 on hot days when energy production prices peak may also add to the burden (personal
64 communication, J. McDill, MARAMA, and A. Mirzakhalili, DE DNREC).
65 Intensified emissions of NO_x will boost the photochemical production of ozone,
66 contributing to the positive value of the CPF.

67 We use data from EPA's Continuous Emission Monitoring System (CEMS) to
68 quantify the temperature sensitivity of power plant emissions of NO_x; the CEMS
69 monitor emissions from a variety of boilers, but the biggest contributors are power
70 generating units, and hereafter we will use the term "power plants emissions" to refer
71 to all sources in the CEMS inventory. The temperature dependence of emissions
72 in the eastern U.S. during summer ($\frac{\partial Emission(NO_x)}{\partial T}$), and the response of ground
73 level NO_x to temperature ($\frac{\partial [NO_x]}{\partial T}$) are derived. We then use measurements from
74 the 2011 National Aeronautics and Space Administration (NASA) Deriving
75 Information on Surface Conditions from COlumn and VERtically Resolved
76 Observations Relevant to Air Quality (DISCOVER-AQ) aircraft campaign in the
77 Baltimore/Washington area to calculate the OPE. Finally, these various factors are
78 used to assess the contribution of the temperature sensitivity of power plant emissions
79 of NO_x to observed CPF in the eastern U.S.
80
81 **2. Data and Methods**
82 Daily CEMS data from power plants in five states of the eastern U.S., Maryland
83 (MD), Ohio (OH), Pennsylvania (PA), Virginia (VA), and West Virginia (WV) were
84 downloaded from the EPA Clean Air Market database (data available at
85 http://ampd.epa.gov/ampd) [*He et al.*, 2013]. We also acquired hourly NO_x
86 observations in the Baltimore/Washington area from the EPA Air Quality System
87 (AQS) website (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm,
88 locations of the selected NO_x monitoring sites are shown in Figure S1 of the auxiliary

89 material). Daily emissions of power plants and surface concentrations of NO_x in
90 summer (June, July, and August) were calculated (see details in [*He et al.*, 2013]).
91 Hourly surface temperature data were obtained from the National Oceanic and
92 Atmospheric Administration (NOAA) National Climatic Data Center
93 (http://gis.ncdc.noaa.gov). Observations from five monitoring sites, the
94 Baltimore/Washington International Airport (BWI), the Cleveland Hopkins
95 International Airport (CLE), the Pittsburg International Airport (PIT), the Dulles
96 International Airport (IAD), and the Yeager Airport (CRW), were selected to
97 represent the local ambient temperature in MD, OH, PA, VA, and WV, respectively.
98 Daily mean temperatures were computed for each site.
99 The proper quantification of the impact of $\frac{\partial[NO_x]}{\partial T}$ on ambient ozone requires
100 accurate knowledge of the OPE, defined as the net number of ozone molecules
101 produced per molecule of emitted NO_x [e.g., *Liu et al.*, 1987; *Kleinman et al.*, 2002].
102 We have estimated OPE from the slope of O_x (O_3 + NO_2) versus NO_z (NO_y – NO_x)
103 [*Kleinman et al.*, 2002] from simultaneous observations of these species. All
104 measurements were obtained by the National Center for Atmospheric Research
105 (NCAR) 4-channel chemiluminescence instrument [*Walega et al.*, 1991] during the
106 DISCOVER-AQ campaign over the eastern U.S. in July 2011 (data archive at
107 http://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq). Our estimate of OPE is
108 restricted to measurements made in the planetary boundary layer (PBL, pressure >
109 890 hPa) that show a strong linear correlation ($r^2 > 0.8$) between O_x and NO_z for
110 individual vertical spiral.

111

112 **3. Results**

113 For each summer between 1997 and 2011, we have tabulated the total number of
114 days with an ozone exceedance in the Baltimore/Washington region, the summertime
115 mean surface ozone abundance in the region, and number of days when temperature
116 exceeded 32.3°C (90°F) (Figure S2 in the auxiliary material). The analysis confirms
117 that ozone pollution during the past 15 years is closely related to ambient temperature.
118 Figure 1 shows daily power plant emissions of NO_x versus surface temperature in MD,
119 with data grouped into four time periods. For all time periods, the power plant
120 emission of NO_x rises with increasing temperature. Power plant emissions decreased
121 significantly after 2002 due to the EPA NO_x SIP call, with widespread
122 implementation of selective catalytic reduction (SCR) removal of NO_x [*He et al.*,
123 2013]. Plots for other states are similar (Figure S3 in the auxiliary material).

124 We next calculated $\frac{\partial Emission(NO_x)}{\partial T}$ using linear regression analysis of daily
125 CEMS NO_x emissions versus daily mean temperature. Figure 2 presents the
126 temperature response of NO_x emissions from power plants (slope) and the correlation
127 coefficient (r). High correlation between NO_x emissions and temperature is
128 observed; except for 2003 in WV, which could be caused by partial implementation of
129 NO_x controls associated with the NO_x SIP call. The value of $\frac{\partial Emission(NO_x)}{\partial T}$
130 averaged for the five states decreased from ~15 tons/°C prior to 2002 to ~8 tons/°C
131 after 2002. The summertime power plant emissions of NO_x in the five states were
132 ~3000 tons/day in the late 1990's and ~1000 tons/day in the early 2010's [*He et al.*,

2013]. Thus, a 1°C temperature increase could have raised emissions of NO_x in the five states considered by ~75 tons prior to 2002 and ~40 tons after 2002, corresponding to increase of ~2.5% and ~4.0%, respectively, with respect to overall emissions of power plants. *He et al.* [2013] reported that ground level NO_x is strongly correlated with power plant emissions of NO_x in the Baltimore/Washington area (Figure S4 in the auxiliary material). Using the slope of the relation between these two quantities, we estimate $\frac{\partial[NO_x]}{\partial T}$ to be ~0.25 ppb/°C prior 2002 and ~0.10 ppb/°C after 2002.

Figure 3 shows the relationship between OPE inferred from DISCOVER-AQ measurements and maximum NO_x observed during each spiral. The average OPE value was ~8 mol/mol in the Baltimore/Washington area in 2011. Using the value of $\frac{\partial[NO_x]}{\partial T}$ given above and assuming that the OPE observed in 2011 is applicable for all years, and formulating the temperature sensitivity of surface ozone to power plant emissions as $\frac{\partial[O_3]}{\partial T} = \frac{\partial Emission(NO_x)}{\partial T} \times \frac{\partial[NO_x]}{\partial Emission(NO_x)} \times OPE$, we estimate $\frac{\partial[O_3]}{\partial T}$ to be ~2.0 ± 1.0 ppb/°C prior to 2002 and ~0.8 ± 0.4 ppb /°C after 2002 (uncertainty analysis is described in the auxiliary material). The decline is due to widespread implementation of SCR technology in power plants after 2002. Bloomer et al. [2009] reported empirical values for the CPF of 3.2 ppbv/°C (prior to 2002) and 2.2 ppbv/°C (after 2002). Hence, the sensitivity of power plant emissions of NO_x to ambient temperature may have contributed ~2/3 of the observed CPF prior to 2002 and ~1/3 of CPF after 2002.

We have assumed that the OPE inferred from DISCOVER-AQ data during

155 summer 2011 applies for all of the time periods under consideration. Tropospheric
156 ozone production is a nonlinear function of the abundance of NO_x and VOCs [e.g.,
157 *Lin et al.*, 1988; *EPA*, 2006]. Observed values of OPE range from 5 mol/mol in
158 urban areas [*Kleinman*, 2000; *Nunnermacker et al.*, 2000] to ~50 mol/mol in the clean
159 marine atmosphere [*Wang et al.*, 1996]. With decreasing trends of ambient NO_x in
160 the eastern U.S. [*He et al.*, 2013], the OPE of ~8 mol/mol may be an overestimate for
161 the late 1990's and early 2000's, because generally OPE falls as NO_x rises [*Kleinman*
162 *et al.*, 2002]. Our estimate that ~2/3 of CPF can be explained by the temperature
163 dependence of power plant emissions prior to 2002 should therefore be treated as an
164 upper limit, since the OPE in the early 2000's was likely lower than that determined
165 from measurements in 2011. Finally, our analysis only considers the temperature
166 dependence of NO_x emissions from power plants equipped with CEMS
167 instrumentation; we do not consider small additional contributions from vehicles and
168 auxiliary electricity generators.
169
170 4. **Concluding Remarks**
171 Emissions of NO_x from vehicles and power plants have declined significantly in
172 the eastern U.S during the past 15 years. Nonetheless, daily emissions of NO_x are
173 tied to electricity demand, which rises on hot days due to increased use of air
174 conditioners. Much of these emissions can be attributed to the less regulated
175 peaking and auxiliary units.. It has long been known that surface ozone tends to be
176 higher on hot summer days. We have shown that for the eastern U.S., a considerable

177 portion (~1/3) of the observed relationship between surface ozone and temperature,
178 termed the CPF, is caused by the increase in power plant emissions of NO_x (an
179 important ozone precursor) on hot summer days. This analysis suggests a substantial
180 part of one danger of climate change, deteriorating air quality, can be mitigated by
181 regional or national regulatory actions to continue to reduce the emission of ozone
182 precursors, i.e., limiting power plant emissions of NO_x on hot days..
183
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191
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Figure 1. Scatter plots of CEMS daily NO_x emissions for MD versus daily mean temperature at BWI airport (summers only). Colors denoted various four year time periods, as indicated.

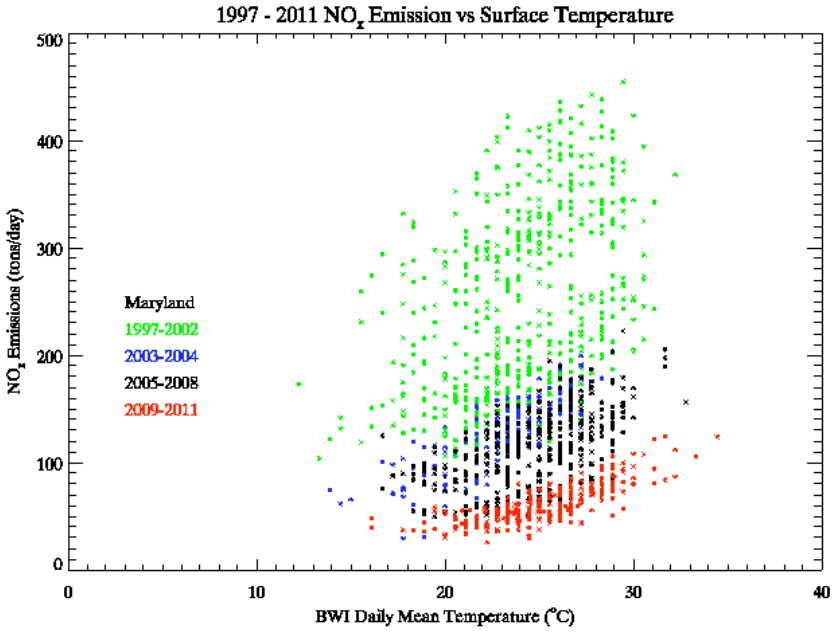
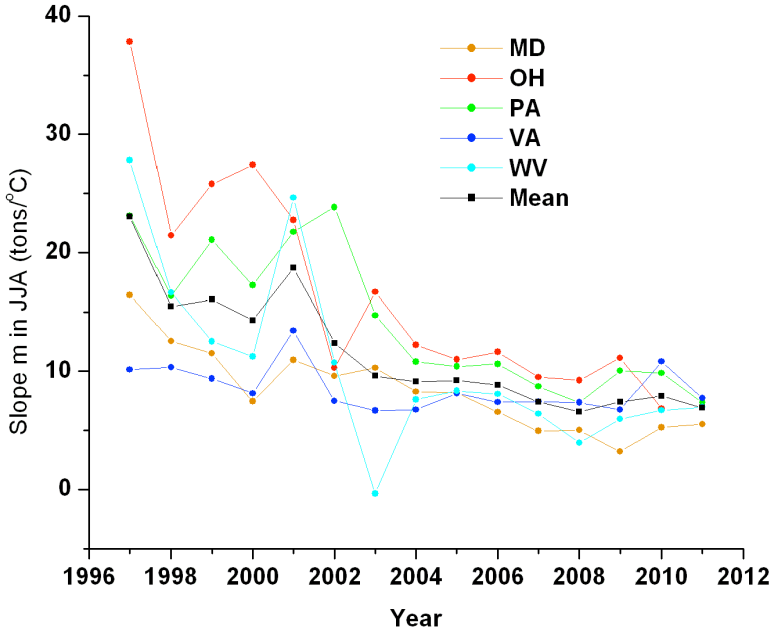


Figure 2. Time series of the temperature sensitivity of power plant emissions of NO_x versus surface temperature. Results of linear regression analysis ($Y = mX + B$, r) of all CEMS and temperature data for individual states and specific years are shown as slope (m) in panel a) and correlation coefficient (r) panel b).

a)



b)

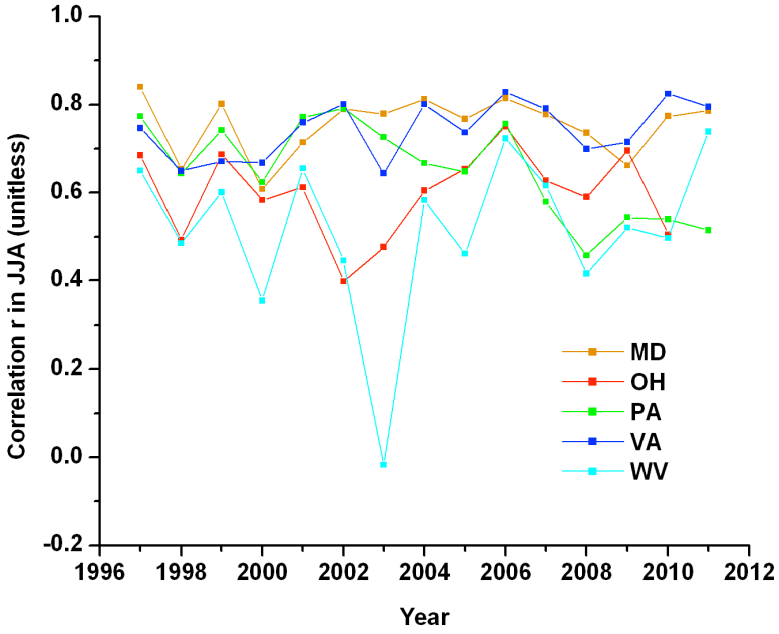


Figure 3. OPE (slope of O_x versus NO_z) versus maximum NO_x during individual spirals in the PBL (p > 890 hPa) during the 2011 DISCOVER-AQ campaign. The red lines denote the mean value of OPE within a specific maximum NO_x bins; the boxes show the 25th and 75th percentiles; and the whiskers represent the 5th and 95th percentiles. OPEs are used only if O_x versus NO_z exhibits a tight correlation (r^2 > 0.8).