

1 **Observed Relationships of Ozone Air Pollution with Temperature**
2 **and Emissions**

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11 Higher temperatures caused by increasing greenhouse gas concentrations are
12 predicted to exacerbate photochemical smog if precursor emissions remain constant. We
13 perform a statistical analysis of 21 years of ozone and temperature observations across
14 the rural eastern U.S. The climate penalty factor is defined as the slope of the
15 ozone/temperature relationship. For two precursor emission regimes, before and after
16 2002, the climate penalty factor was consistent across the distribution of ozone
17 observations. Prior to 2002, ozone increased by an average of ~3.2 ppbv/°C. After 2002,
18 power plant NO_x emissions were reduced by 43%, ozone levels fell ~10%, and the
19 climate penalty factor dropped to ~2.2 ppbv/°C. NO_x controls are effective for reducing
20 photochemical smog and might lessen the severity of projected climate change penalties.
21 Air quality models should be evaluated against these observations, and the climate
22 penalty factor metric may be useful for evaluating the response of ozone to climate
23 change.

24 **1. Introduction**

25
26 Power plant NO_x emissions decreased by 43% for the time period 1989-1998
27 compared to 2003 to 2007 as a result of air pollution control programs in the eastern
28 United States [Kim et al., 2006, Bloomer, 2008.] Emissions from automobiles and
29 industrial activity have essentially remained constant, as indicated from satellite
30 observations of tropospheric NO₂ [Kim et al., 2006]. Early indications from ambient
31 monitoring networks and atmospheric chemical transport models provide evidence
32 that ozone amounts have declined as a result of declining power plant emission
33 [Gégo et al., 2007 and 2008].

34 Temperature can be used as a surrogate for the meteorological factors
35 influencing surface ozone formation [Jacob et al., 1993, Ryan et al., 1998, Camalier et
36 al., 2007]. Temperature has been rising, on average, in the eastern U.S. [IPCC, 2007].
37 Surface ozone is expected to rise, all else being equal, with an increase in
38 temperature [EPA, 2006]. The ozone temperature relationship has been
39 investigated in the past [Sillman and Samson, 1995; Sillman, 1999]. However,
40 questions remain regarding how this relationship changes over time, by location,
41 and with precursor emissions.

42 Modeling studies suggest a penalty in ozone air quality resulting from
43 forecast climate changes. Wu et al. [2008] forecast a penalty of 2 to 5 ppbv in daily
44 maximum 8-hour averaged surface ozone amounts in parts of the eastern U.S.,
45 offsetting expected air quality improvement from emission reductions, between
46 2000 and 2050. Jacob and Winner [2009] provide a review of recent modeling of air
47 quality changes under various scenarios of forecasted global climate change and

48 indicate a climate change penalty from 1 to 8 ppbv ozone is likely in the eastern U.S.
49 this century.

50 Air quality models need evaluation using observations to assess model
51 performance and to establish confidence in the effect of climate change on surface
52 ozone. Areas with rising temperatures and precursor emissions are projected to
53 suffer the consequences of worsening air pollution including increases in mortality
54 and morbidity [*Bell et al., 2005, NRC 2008*] along with significant damage to crops
55 [*Ellingsen et al., 2008*].

56 Here we investigate observational data obtained in the rural eastern U.S.
57 over the last 21 years. Specifically, we examine hourly ozone and temperature
58 relationships measured by the CASTNET network. We group the data into four
59 chemically coherent receptor regions. We investigate the ozone vs. temperature
60 relationship for each receptor region, for two time periods characterized by
61 differing power-plant emissions: before and including 2002 and after 2002. The
62 analysis shows a consistent ozone temperature relationship across the eastern U.S.
63 and that the slope of the relationship decreases after the power-plant emissions
64 reductions.

65 66 **2. Measurements and Statistical Method**

67 68 **2.1 NO_x emissions**

69 NO_x emissions from power plants were historically estimated from fuel
70 sampling and analysis methods. Since 1995, continuous emission monitoring
71 equipment has been operating in the exhaust gas stream of the largest fossil fuel
72 fired plants nationwide. Care must be used in assessing NO_x emission from power

73 plants when combining data sources and when using emissions numbers from
74 government databases. We have analyzed the historical trend of ozone season (1
75 May to 30 September) NO_x emission from power plants and conclude two distinct
76 emission regimes can be constructed [see also *Bloomer*, 2008].

77 Power plant NO_x emissions (Figure 1) decreased as a result of air pollution
78 control programs in the eastern United States by 43%, on average, around 2002.
79 Emissions from automobiles and industrial activity have essentially remained
80 constant [*Kim et al.*, 2006]. Using the power plant emission changes to define two
81 distinct emission regimes, we assign the period prior to and including 2002 to one
82 regime and the period after the 43% reduction to a post 2002 emission regime.

83 **2.2 Surface Ozone and Temperature Observations**

84 Co-located, rural observations of ozone concentration and temperature are
85 collected by the Clean Air Status and Trends Network (CASTNET), operated by the
86 U.S. EPA since 1987 (<http://www.epa.gov/castnet>) and described by *Clarke et al.*
87 [1997]. All ozone and temperature data presented here are simultaneous, hourly
88 averages from the ozone season; only data simultaneously labeled valid by the
89 CASTNET team were accepted. Temperature is observed with platinum wire
90 resistance thermometers or thermistors and ozone amounts are measured using a
91 UV absorbance method. Observations analyzed here span the ozone seasons from
92 1987 until 2007.

93 **2.3 Statistical Approach**

94 We aggregate CASTNET sites into four chemically coherent regions after the
95 results of *Lehman et al.* [2004] and the two time periods noted above. This method
96 yields a large number of observations for analysis with over 3 million

97 simultaneously valid observations of temperature and ozone across the eastern U.S.
98 For example, the resulting data set for the Mid-Atlantic region includes 1,196,350
99 individual valid observations of concurrent temperature and ozone, with 343,398
100 observations after 2002, and 852,952 from 1987 up to and including 2002
101 [Bloomer, 2008].

102 We used the exploratory data analysis techniques described by Wilks [2006].
103 In general, parametric tests rely on strict assumptions about the probability
104 distribution of the data; such as assuming the distribution is Gaussian. In our study,
105 we do not make these assumptions because more general and conservative
106 conclusions are possible. The shapes of the full ozone and temperature
107 distributions have little documentation in the literature. Non-parametric methods
108 are more robust and resistant to influence from outliers due to instrument error or
109 anomalous conditions. Further details are given in the auxiliary material¹.

110 **3. Results and Discussion**

111 The hourly ozone concentrations (including nighttime observations)
112 dropped by about 10% in the Mid-Atlantic and Northeast regions across the full
113 distribution (Figure 2). Ozone in the Great Lakes and Southwest regions decreased
114 post-2002 by larger relative amounts in the upper and lower percentiles. A similar
115 reduction is seen in the subset of observations made during daytime hours.
116 Sampling the daily maxima for one-hour and 8-hour averages (time periods of
117 interest due to their specification by EPA in the National Ambient Air Quality
118 Standards for ozone) shows large decreases at all locations in the distribution. The
119 largest decreases in ozone occur at the highest concentrations. Ozone in the 95th
120 percentile of the 8-hour average daily maxima in the Mid-Atlantic declined 15.6

121 ppbv after 2002. This observational evidence supports conclusions previously
122 reported from modeling studies [*Gégo et al.*, 2007 and 2008].

123 The ozone concentration (Figure 2) shows decreases across the entire
124 distribution of observed values, pre- to post-2002, for all regions. The figure shows
125 the amount of ozone at each location statistic of the 5th, 25th, 50th, 75th and 95th
126 percentiles occurring prior to and including 2002 (horizontal placement) as well as
127 the change in ozone for each percentile (vertical extent).

128 Temperature distributions (Figure 2) show that air warmed across the Great
129 Lakes and Mid-Atlantic regions after 2002. Mid-Atlantic temperatures increased the
130 most, especially over the lower portion of the distribution. The median temperature
131 differences are 0.51°C for pre to post-2002 and 0.68°C pre-1999 to post-2002.
132 These are consistent with published estimates of 0.25 to 0.30°C/decade for
133 observed temperature trends for similarly defined regions of the eastern U.S. [*IPCC*,
134 2007]. The Mid-Atlantic region has temperature differences larger than those
135 predicted from a global greenhouse gas forcing alone [*IPCC*, 2007], indicating a
136 regional source of warming due to factors that may not be represented in current
137 global modeling simulations.

138 To investigate further the observational data for a relationship between
139 ozone and temperature, we construct conditional ozone distributions corresponding
140 to specific temperature ranges (Figure 3.) For all regions, at all times, in any
141 location within the distribution, ozone concentrations increase with increasing
142 temperatures. The spread in the data as a function of temperature shows how other
143 variables influence ozone at a given temperature. This relationship between the

144 location statistics (e.g., the 50th or 75th percentile values) and temperature reveals a
145 consistently strong dependence of ozone on temperature, regardless of where the
146 distribution is sampled. This approach differs distinctly from filtering the
147 observations by choosing daily maximum 1-hr or 8-hr averages prior to examining
148 the ozone vs. temperature relationship. The strength of the temperature
149 relationship is reinforced by the consistency across the percentiles and the relative
150 insensitivity of the relation to temperature bin size [see also *Bloomer, 2008*]. Our
151 conclusions are insensitive to the precise choice of year to delineate emission
152 regimes, reflecting the transition period for emission reductions between 1998 and
153 2002 (see auxiliary material¹).

154 The ozone-temperature relationship is linear in all four regions before and
155 after 2002 over the temperature range of 19 to 37°C. A linear fit of ozone vs.
156 temperature yields nearly the same slope, regardless of which percentile is chosen
157 for the Great Lakes, Northeast, and Mid-Atlantic regions (Figure 3). The average of
158 the slopes of the five linear fits in the Mid-Atlantic region for data collected prior to
159 2002, corresponding to the 5th, 25th, 50th, 75th and 95th percentiles, is 3.3 ppbv O₃/°C,
160 with a minimum of 3.2 and a maximum of 3.5 ppbv O₃/°C. The slope decreases to an
161 average of 2.2 ppbv O₃/°C after 2002, with a similarly small range of 1.9 to 2.6 ppbv
162 O₃/°C. The post-2002 data show less ozone compared to the pre-2002 data at the
163 higher temperatures, indicating ozone production became less sensitive to
164 temperature increases after the 2002 emission reductions.

165 We define a climate penalty factor as the slope of ozone vs. temperature.

166 This factor, combined with knowledge of temperature change, allows one to

167 quantify a relationship indicative of future change in air quality due to warming.
168 Theory must be developed and model calculations must be conducted to assess how
169 the observed CPF relates to future conditions as well as other regions. The climate
170 penalty factor is remarkably similar across the Great Lakes, Northeast and Mid-
171 Atlantic regions, with an average slope for the three regions of 3.2 ppbv O₃/°C
172 (range: 3.0 to 3.6 ppbv O₃/°C) prior to 2002 and 2.2 ppbv O₃/°C (range: 2.0 to 2.5
173 ppbv O₃/°C) after 2002.

174 In the Southwest region ozone decreased after 2002, but the climate penalty
175 factor remained nearly the same. Ozone production in the Southwest region differs
176 from the other regions of our study in that petrochemical and vehicular emissions
177 dominate; the air is rich in highly reactive hydrocarbons. Advection from power
178 plants may play a smaller role, but observations are relatively sparse and results are
179 less robust. . The Southwest region shows a small increase in the climate penalty
180 factor after 2002, with values going from 1.3 ppbv/°C (range: 1.1 to 1.5 ppbv/°C)
181 before 2002 to 1.4 ppbv/°C (range: 1.1 to 1.9 ppbv/°C) after 2002 (Figure 3).

182 The decrease in ozone concentration and decline in the climate penalty factor
183 observed for the Mid-Atlantic, Great Lakes and Northeast regions after 2002 are
184 statistically significant. Both parametric and non-parametric techniques were
185 applied for determining the significance of the differences in ozone, temperature,
186 and the climate penalty factor as discussed above. Distributions of ozone and
187 temperature were compared to parameterized distributions. The distributions are
188 normal in the middle quartiles, departing significantly from normal at higher ozone
189 values; therefore, we opted to use non-parametric techniques for robust results.

190 Wilcoxon-Mann-Whitney hypothesis testing was performed, and all differences
191 discussed above are highly significant; the probability of falsely rejecting the null
192 hypothesis of no difference is less than 0.001.

193 This level of significance was observed for the vast majority of the data. For
194 example, in the Mid-Atlantic region, over 950,000 observations, or more than 80%
195 of the total data, fall between 15 and 37°C. The significance of the difference in
196 ozone and the climate penalty factor broke down only for the highest temperatures
197 of greater than 37°C. These observations represent less than 100 data points, a
198 small fraction of the total. Given the known temporal autocorrelation that exists on
199 the scale of hours to days in the data, we opted to develop additional robust and
200 resistant non-parametric estimates of the standard error for the location statistics,
201 and used these estimates to determine significance as well. We have consistently
202 tended toward overestimating the standard error in our statistical analyses, which
203 provides for great confidence in the statistical significance (meaning differences
204 larger than the combined standard error in this case) of the changes in ozone,
205 temperature, and the climate penalty factor for the Mid-Atlantic, Great Lakes, and
206 Northeast regions. Further details of the statistical significance are given in the
207 auxiliary material¹.

208

209 **4. Concluding Remarks**

210 Our analysis indicates that the climate change penalty in air quality
211 decreases when ozone precursor emissions are reduced, as suggested by modeling
212 studies [e.g., *Wu et al.*, 2008]. The slope of the ozone temperature relationship,
213 sampled at the various location statistics of the full distribution, was 3.2 ppbv O₃/°C

214 (range: 3.0 to 3.6 ppbv O₃/°C) prior to 2002 and decreased to 2.2 ppbv O₃/°C (range:
215 2.0 to 2.5 ppbv O₃/°C) after 2002, coincident with the 43% reduction in power plant
216 emission of NO_x. Assuming that NO_x emissions continue to fall, ground level ozone
217 and the climate penalty factor in the eastern U.S. should continue to improve. In
218 regions of increasing NO_x emissions, including much of the developing world
219 [Richter *et al.*, 2005], ozone will increase more than expected (based upon emissions
220 alone) if temperatures also rise. Predicted rising temperatures [IPCC, 2007] bode ill
221 for air quality and human health [NRC, 2008; West *et al.*, 2006], unless substantial
222 NO_x emission reductions are implemented. The climate penalty factor is of
223 significant concern to affected populations and should be evaluated for more
224 regions of the globe. The climate penalty factor can be combined with estimates of
225 future temperature increases to quantify possible impacts of warming on air quality.
226 The climate penalty factor provides a means for assessing the ozone/temperature
227 relationship of air quality models for present day conditions. Proper representation
228 of this relationship would provide confidence in the accuracy of simulations of the
229 impacts of climate change on future air quality.

230

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235

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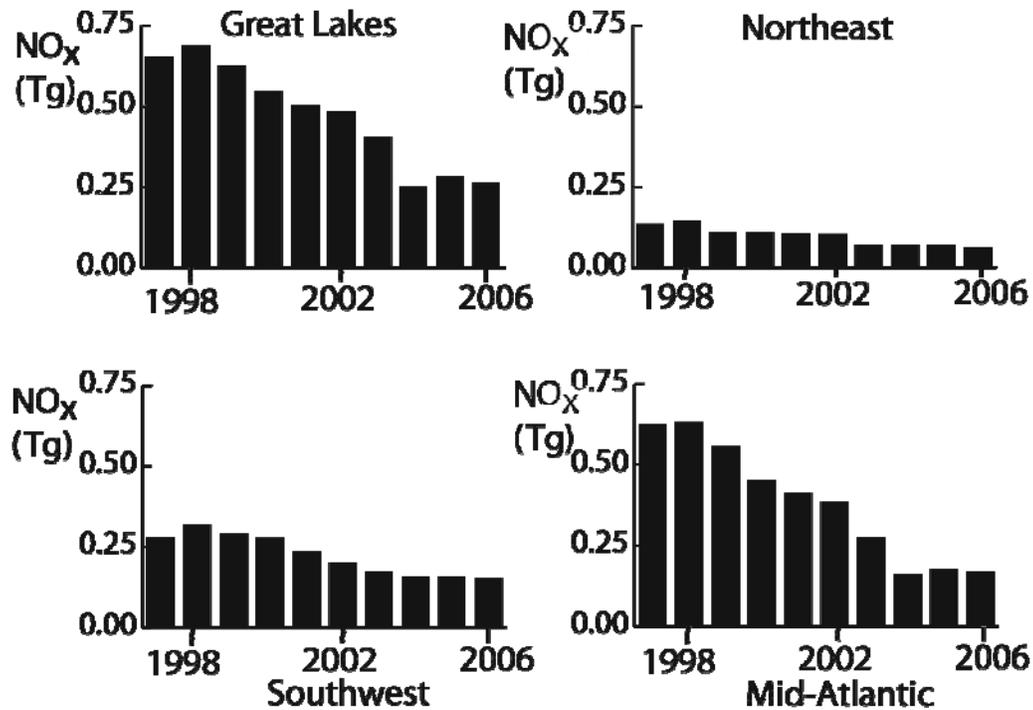
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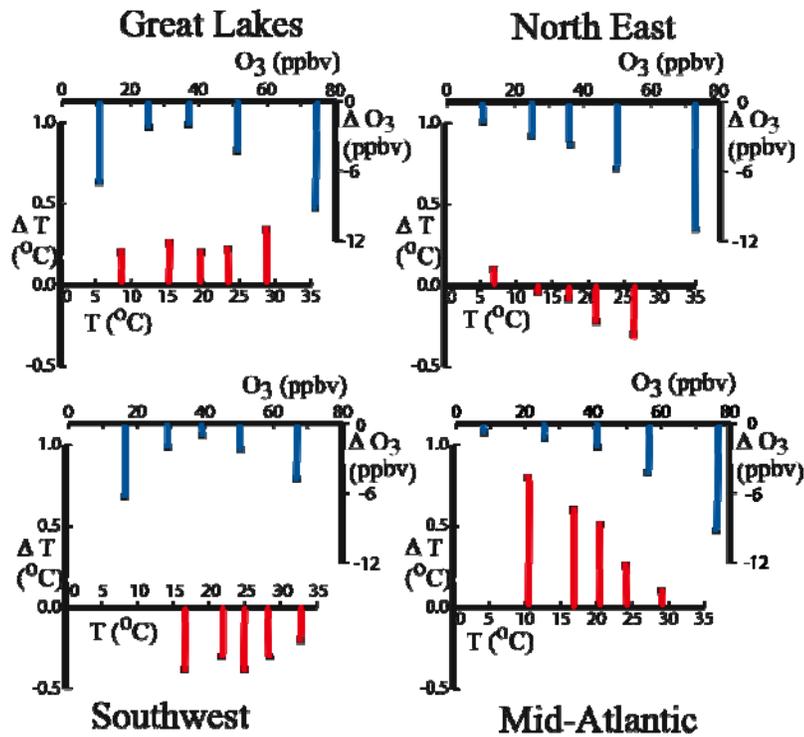
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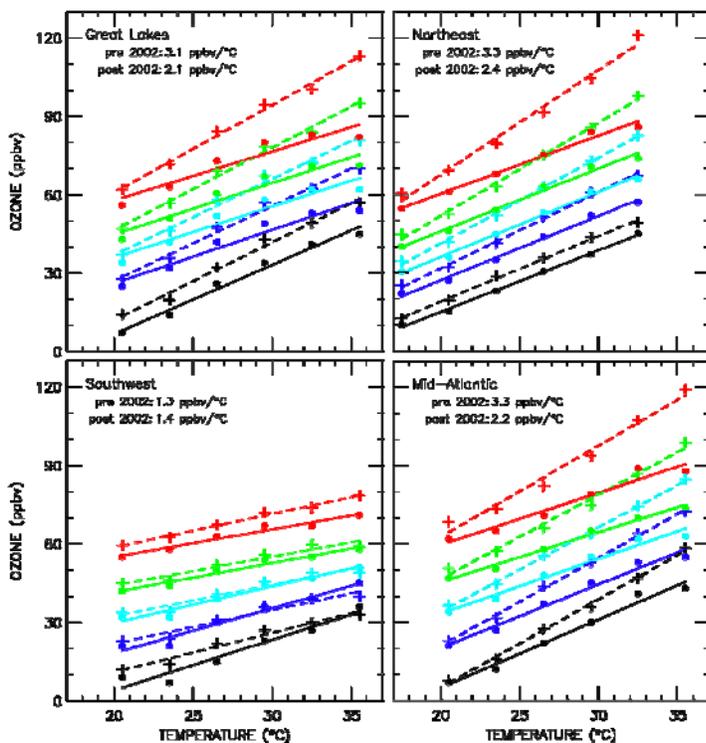


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Figure 1. Power plant ozone season (May to September) NO_x emissions (as Tg NO₂ where 1 Tg NO₂ is equivalent to 0.304 Tg N) aggregated by region and year. Regions are determined after *Lehman et al*, [2004] representing chemically coherent receptor regions for ozone air pollution.



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 295
 296 Figure 2. Hourly ozone and temperatures for ozone seasons, aggregated into
 297 chemically coherent receptor regions in the eastern U.S. after *Lehman et al.* [2004]
 298 as observed by rural ambient monitoring stations of the CASTNET network. The
 299 blue bars at the top of each panel represent the amount of change each location
 300 statistic for ozone underwent after 2002. The red bars at the bottom of each panel
 301 represent the amount temperature changed, after 2002 compared to the hourly
 302 observations obtained between 1987 and 2002. The horizontal position of the bars
 303 represents the value of ozone (blue) and temperature (red) for the pre-2002 value
 304 of each location statistic, going from left to right in this order: 5th, 25th, 50th, 75th, and
 305 95th percentiles of the full distribution. This graphical representation allows for the
 306 reconstruction of the two distributions (pre-2002 and post-2002) for each region
 307 for both ozone and temperature. For example, the Mid-Atlantic 5th percentile
 308 temperature prior to 2002 was 10°C, and rose by 0.8°C after 2002; the 95th
 309 percentile ozone abundance in the Mid-Atlantic was 76 ppbv, and declined by 9
 310 ppbv after 2002.



311

312 Figure 3. Ozone vs. temperature plotted for 3°C temperature bins across the range
 313 19 to 37°C for the 5th, 25th, 50th, 75th and 95th percentiles of the distributions before
 314 and after 2002 in chemically coherent receptor regions.. Color corresponds to
 315 percentile (red is 95th, green is 75th, light-blue is 50th, dark blue is 25th, and the
 316 black line is the 5th percentile value.) Dashed lines are for the pre-2002 linear fit of
 317 ozone as a function of temperature at the percentile indicated by the color. Solid
 318 lines correspond to the linear fits after 2002. Solid circles indicate the data points in
 319 the post 2002 time period, and “plus” signs indicate the pre-2002 values. Values are
 320 plotted at the mid-point temperature of the 3°C temperature bin. The average slope
 321 given on each panel, indicates the climate penalty factor.
 322
 323