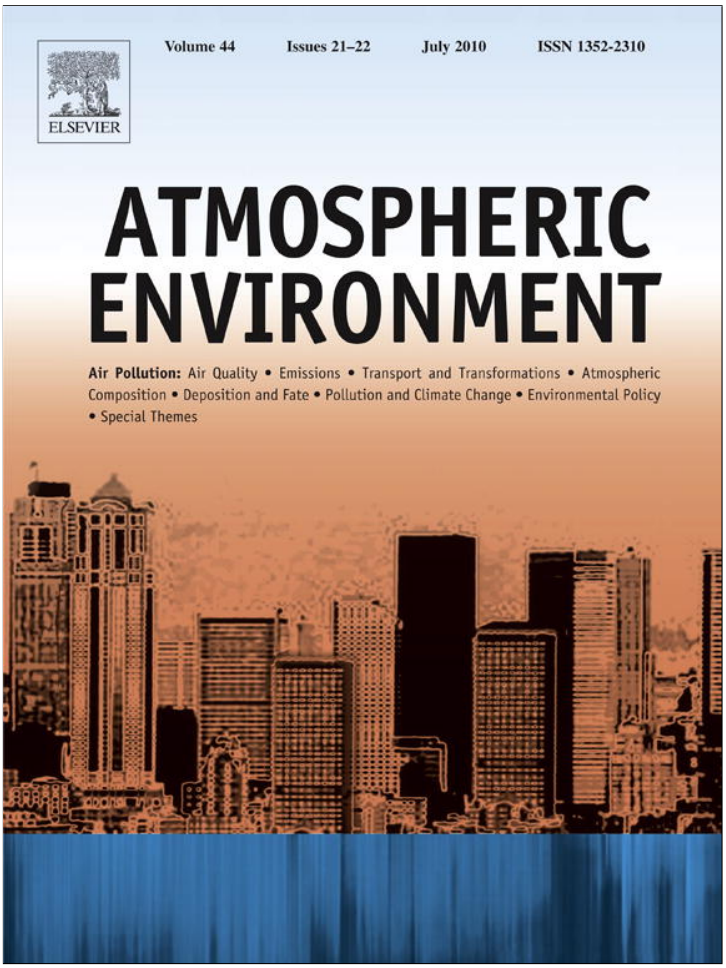

Atmospheric Environment 44 (2010) 2543–2551

Contents lists available at ScienceDirect

Atmospheric Environment

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

Changes in seasonal and diurnal cycles of ozone and temperature in the eastern U.S.

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ARTICLE INFO

Article history:
Received 16 December 2009
Received in revised form
8 April 2010
Accepted 13 April 2010

Keywords:
Ozone
Weather
Air pollution
Temperature
Climate change
Trends

ABSTRACT

The pollutant tropospheric ozone causes human health problems, and environmental degradation and acts as a potent greenhouse gas. Using long-term hourly observations at five US air quality monitoring surface stations we studied the seasonal and diel cycles of ozone concentrations and surface air temperature to examine the temporal evolution over the past two decades. Such an approach allows visualizing the impact of natural and anthropogenic processes on ozone; nocturnal inversion development, photochemistry, and stratospheric intrusion. Analysis of the result provides an option for determining the duration for a regulatory ozone season. The application of the method provides independent confirmation of observed changes and trends in the ozone and temperature data records as reported elsewhere. The results provide further evidence supporting the assertion that ozone reductions can be attributed to emission reductions as opposed to weather variation. Despite a ($\sim$0.5 °C decade^{-1}) daytime warming trend, ozone decreased by up to 6 ppb decade^{-1} during times of maximum temperature in the most polluted locations. Ozone also decreased across the emission reduction threshold of 2002 by 6–10 ppb indicating that emission reductions have been effective where and when it is most needed. Longer time series, and coupling with other data sources, may allow for the direct investigation of climate change influence on regional ozone air pollution formation and destruction over annual and daily time scales.

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1. Introduction

Both emissions and weather affect surface ozone amounts. Assessment of pollution abatement strategies requires separation of these two factors. Methods to determine whether emissions controls improve air quality when it matters most (during sustained pollution episodes in spring and summer) and to quantify surface ozone concentration changes and how they respond to emissions and weather during other periods are required (U.S. EPA, 2006).

Ozone in the troposphere can arise from a natural process of downward transport from the stratosphere, but *in situ* photochemical production resulting from anthropogenic precursor emissions dominates globally. Pollution ozone is formed in a mixture of reactive nitrogen oxides (NOx) and volatile organic compounds reacting in the presence of sunlight; NOx is usually the limiting ozone precursor. Reactions with HOx, dry deposition and titration with NO remove ozone.

$$NO + O_3 \rightarrow NO_2 + O_2$$

The NO_2 thus produced acts as a nighttime reservoir and ozone is reformed in the morning as photolysis resumes.

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2\,(+M) \rightarrow O_3\,(+M)$$

Recently, the reaction of nitrogen dioxide with ozone to produce the nitrate radical, and subsequent reactions with volatile organic compounds (VOC) to produce organic nitrogen compounds, such as alkyl nitrates, have been recognized as important reservoirs of NOx (e.g., Duce et al., 2008).

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

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1352-2310/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2010.04.031

$NO_3 + VOC \rightarrow R\text{-}ONO_2$

These organic nitrogen compounds are sometimes lost from the atmosphere to wet and dry deposition, but a substantial fraction remains airborne where reactions such as photolysis, and attack by OH, can release NOx to produce ozone. Thus alkyl nitrates and related compounds sequester NOx in a manner similar to peroxy acetyl nitrate (PAN), a species long known to play a role in the spring ozone maximum at high latitudes (e.g., Brich et al., 1984; Dickerson, 1985); notably PAN thermal decomposition effectively stops in the Arctic winter.

A positive correlation between ozone and temperature arises from a combination of meteorological and chemical factors – some coincidental and some causal. High temperatures lead to high concentrations of ozone precursors from the dissociation of PAN, greater electrical energy use, and from biogenic emissions of isoprene. Both high temperatures and high pollution concentrations are associated with synoptic high pressure systems and sunny (with fast photolysis rates) stagnant conditions. During the warmest time of the day, the depth of the planetary boundary layer (PBL) reaches its maximum and entrains O_3 from the residual layer aloft. During the coolest time of the day, just before dawn, the PBL reaches its minimum, leading to rapid loss of O_3 due to dry deposition and sequestration as NOx; there is no sunlight to reform O_3. The relationship between ozone and temperature is thoroughly discussed in the Criteria Document for Ozone and Related Photochemical Oxidants (U.S. EPA, 2006).

Previous modeling work showed that control of NOx emissions from power plants lowered ozone concentrations substantially (Frost et al., 2006; Gégo et al., 2007; 2008; Gilliland et al., 2008; Godowitch et al., 2008a,b; Hudman et al. 2009). Bloomer et al. (2009) showed that temperature is a useful surrogate for weather variables associated with ozone levels over the past two decades and that a linear relationship exists over the Eastern US in a temperature range of 20–35 °C. Although ozone concentrations at all points in the statistical distribution increased with increasing temperature, the rate of increase weakened in a lower NOx regime. Camalier et al. (2007) use statistical methods to evaluate the long-term influence of weather variables upon ozone formation and reconstruct trends by adjusting the observed surface ozone observations using the observed weather to arrive at an ozone air pollution trend "adjusted" for weather.

Here we use more comprehensive data, and adapt a technique, previously used with success to analyze traditional climate variables, to study tropospheric ozone. The goals are to separate the impact of changes in precursor emission from the influence of changes in weather on daily to seasonal time scales and to show graphically the influences of meteorological and chemical processes on ozone concentrations. Relevant variables include temperature, actinic flux, and atmospheric dynamical effects, such as PBL height, and spring-time stratospheric intrusions.

2. Data

The Clean Air Status and Trends Network (CASTNET) is a rural ambient air monitoring network operated by the US EPA (Clarke et al., 1997). CASTNET temperature measurements are obtained with platinum wire resistance thermometers or with thermistors systematically calibrated to a required absolute accuracy of 0.5; precision is better. Ozone UV absorbance measurements are required to be within 10% when compared with NIST traceable standards. (http://www.epa.gov/castnet/docs/qapp_v41/QAPP_v41_Main_Body.pdf) 1989–2007 observations of five stations located across the eastern US (Table 1) are analyzed here. For these CASTNET sites, 1989–2007 hourly ozone mixing ratios and surface air temperature have been downloaded from the EPA website at (http://www.epa.gov/castnet) and screened for validity using the screening codes provided along with the data.Station Data are in Table 1.

Table 1
CASTNET stations used in the statistical analysis of diel and annual cycles.

Station	State	Latitude (deg)	Longitude (deg)	Elevation (m)
Woodstock	NH	43.94	−71.70	258
Connecticut Hill	NY	42.40	−76.65	501
PennState	PA	40.72	−77.93	378
Beltsville	MD	39.02	−76.81	46
Georgia Station	GA	33.17	−84.40	270

3. Method

Changes in climate may manifest themselves as changes not just in the mean state, but also in variability or in diel or seasonal cycles. In other words climate is more than the average of weather variables. The technique we apply, originally developed to analyze seasonal and diel variations in climate (Vinnikov et al., 2002a,b), will here be employed to study variations in ozone concentrations. The main simplification in this technique is that the seasonal variation of the climatic or environmental variables for a specific hour of observation is approximated by a limited number of Fourier harmonics of an annual period. The number of these harmonics usually should not be less than two but can be larger if necessary. It is also assumed that observed variables may have linear or polynomial trends that can be different in different seasons, but can be approximated by a limited number of Fourier harmonics of the annual cycle. By doing this analysis for each hour of the day across the full data record, we can reconstruct the long-term trends in the diel cycle as well.

Following Vinnikov et al. (2002b), let us consider the observed value of a meteorological variable $y(t,h)$ at day number $t = t_1, t_2, t_3, \ldots, t_n$ and at specific observation times h, ($h = 0, h_1, h_2, h_3, \ldots, H$, $H = 24$ h), as a sum of the expected value $Y(t,h)$ and anomaly $y'(t,h)$ such that:

$$y(t,h) = Y(t,h) + y'(t,h) \tag{1}$$

Supposing that the climatic trends in the time interval (t_1,t_n) are linear, but assuming they are different for different t and h leads to the following:

$$Y(t,h) = A(t,h) + B(t,h)\cdot t \tag{2}$$

where $A(t,h)$ and $B(t,h)$ are periodic functions of the annual period $T = 365.25$ days:

$$A(t,h) = A(t+T,h), B(t,h) = B(t+T,h).$$

For each specific observation time ($h = \text{const}$) periodic coefficients in (2) are approximated as follows:

$$\begin{aligned} A(t,h) &= \alpha_0(h) + \sum_{k=1}^{K}\left[a_k(h)\sin\left(\tfrac{2\pi kt}{T}\right) + b_k(h)\cos\left(\tfrac{2\pi kt}{T}\right)\right], \\ B(t,h) &= \alpha_0(h) + \sum_{m=1}^{M}\left[a_m(h)\sin\left(\tfrac{2\pi mt}{T}\right) + \beta_m(h)\cos\left(\tfrac{2\pi mt}{T}\right)\right]. \end{aligned} \tag{3}$$

The unknown coefficients in (2)–(3) for each h can be estimated from the least squares condition:

$$\sum_{t=t_1}^{t_n}[y(t,h) - Y(t,h)]^2 = \min. \tag{4}$$

Vinnikov et al. (2002b) discuss the choice of K and M. These parameters should be chosen from independent considerations or they can be estimated from analyses of the data. The linear trend for each day of a year is $B(t,h)$. The estimates of time dependent expected value $Y(t,h)$ has a leap-year cycle and this has to be taken into account when interpreting.

We applied this method, first of all, to the full period of ozone and surface air temperature records (18 years of data) using four harmonics of the annual period to approximate seasonal variations in mean value and linear trend at each hour of a day (e.g., $K = M = 4$). The standard error of a trend estimate depends on the number of independent observations and the standard deviation of the ozone residuals (the second column in Fig. 2). The number of independent observations is substantially fewer than the total number of hourly data in each season at each station. Autocorrelation due to synoptic-scale ($\sim$3 d) weather variability decreases the number of degrees of freedom. After accounting for all these effects, the largest of trends in Fig. 2 still differ from zero with a probability greater than 95%. All five independent CASTNET stations display almost the same seasonal and diurnal patterns of trend in ozone concentration, further increasing the statistical significance of our trend estimates.

As an alternative to assuming a linear trend we compare mean values between two periods, 1989–1998, before a 43% average NOx reduction at power plants (Bloomer et al., 2009), and for the period 2003–2007, after the emission reduction. The mean values for the respective time periods have been estimated from the data by assuming that the trend term in (2) is equal to zero, $B(t,h) = 0$.

Plots are constructed to evaluate seasonal and diel cycle, along with the long-term trends, by taking the case that If $B(t,h) = 0$ (meaning there is no trend in this case across the years in the data set at a given observation hour) then average $= A(t,h)$ can be plotted in contour plots as seen in Figs. 1, 3, and 5. When a linear trend term exists at a given hour across the data set (when $B(t,h)$ is not equal to zero) then the expected value is a function of time and the average can be represented by $Y(t,h) = A(t,h) + B(t,h)t$ computed for the middle year of the time interval represented in the complete data set (as in Figs. 2 and 4) in the case where the average is just $A(t)$ when $t = 0$ is chosen to be at the beginning of this middle year.

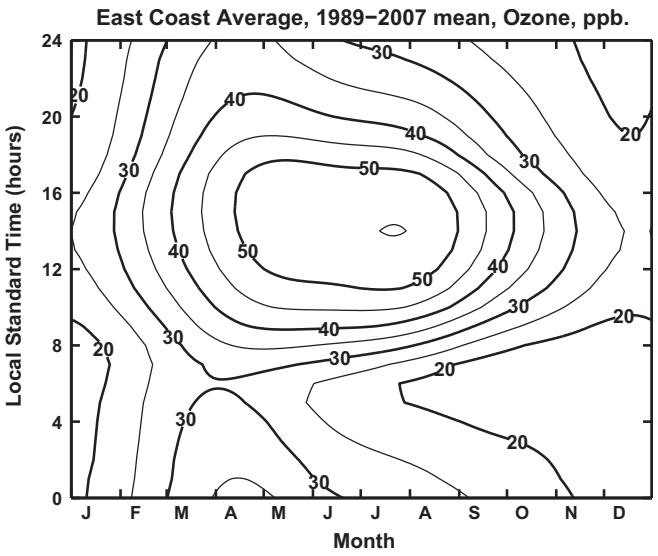

Fig. 1. Average diel (daily) and seasonal distribution of 1989–2007 ozone concentrations observed at five rural eastern US monitoring stations of the CASTNET network contour plotted across local standard time and month. The X-axis depicts season while the Y-axis shows the daily cycle. Ozone demonstrates a distinct maximum in the afternoon of summer days, with a secondary maximum in spring. Local photochemical smog production drives the summer maximum, but downward mixing from the stratosphere as well as free tropospheric production from long-lived precursors contribute to the spring maximum. The minima are seen at night in winter when photochemical production is slow and losses through dry deposition and titration with NO dominate.

4. Results: seasonal and diel variations, trends of ozone and temperature

To characterize the eastern US as a whole, data from all five sites were averaged and analyzed for the entire time period available 1989–2007, (Fig. 1). Seasonal variations (month) follow the X-axis while diel variations (hour of the day) follow the Y-axis. The contours indicate smoothed, mean ozone concentrations (ppb) from the Fourier harmonics. The impact of photochemistry and weather can be readily discerned. The principal maximum occurs in summer, afternoon when photochemical production is fast. A secondary maximum is seen in the spring afternoon, resulting from a combination of stratospheric intrusions and release of NOx from reservoir species such as PAN and alkyl nitrates that build up over the winter at high latitudes. Minima occur at night, or early morning hours in winter, when photochemical production is negligible and the boundary layer is shallow. Both dry deposition and titration with NO remove ozone. Results for specific sites and time periods are depicted in a similar manner in Figs. 2–5.

At the individual sites, ozone (Fig. 2) and temperature (Fig. 4) generally demonstrate characteristic diel and seasonal patterns with maxima on spring or summer afternoons and minima in the early morning hours of winter. Starting with Fig. 2, the contours in the left-most panels indicate 1989–2007 mean ozone concentrations; the center panels display the standard deviation of the detrended ozone observations, indicating the variability in the observed data for each hour and month of the year. The panels on the right indicate the linear trend estimates $B(t,h)$ obtained from the hourly ozone observations in units of ppb per decade. Over the decades of observations considered in this study, concentrations at all sites decreased in summer afternoons; at some sites they increased in winter.

Attempting to depict the effectiveness of pollution control efforts, we separate the data into time periods of greater and lesser NOx emissions. Fig. 3 shows the diel and seasonal distribution of observed mean ozone concentrations at the same five stations for the period 1989–1998 (left panel), before a 43% NOx emission reduction at power plants (Bloomer et al., 2009) and for the period 2003–2007, after the emission reduction (center panel). The panels on the right indicate the difference between mean ozone concentrations for these two periods.

Analogous results for surface air temperature (Figs. 4 and 5) show the diel and seasonal distributions of the multi-year mean values and linear trends at the same rural monitoring stations across the eastern U.S. The 1989–2007 mean temperature (left panels Fig. 3) shows the summer afternoon maxima and winter morning minima. The center panels display the standard deviation of the detrended surface temperatures, indicating the variability of the observed data for each hour and month of the year. The panels on the right indicate the observed 1989–2007 linear trend estimates.

Fig. 5 shows the diel and seasonal distribution of observed mean surface temperatures at the five monitoring stations for the two periods selected for emissions reductions, 1989–1998, and 2003–2007. The left panels display temperatures before the NOx emissions controls, the center panels display temperatures after the emission reduction, and the right panels indicate the differences. In general, over the past few decades winter and spring

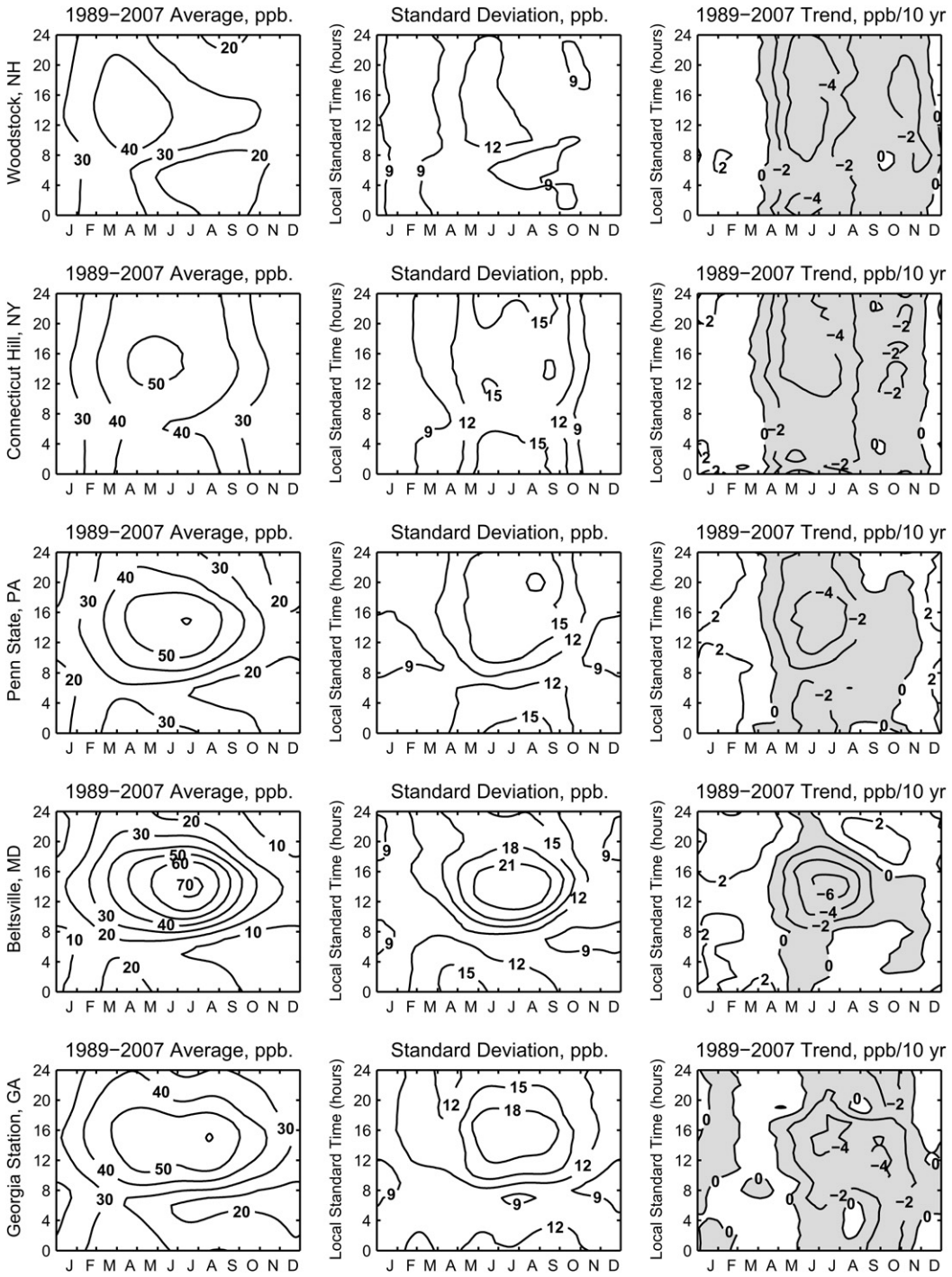

Fig. 2. Diel and seasonal distribution of 1989–2007 means, standard deviations and linear trends of ozone concentrations observed at five rural eastern US monitoring stations of the CASTNET network contour plotted across local standard time and month. Decreases and negative values are shaded. Note that the most polluted sites (Beltsville and Penn State) show the greatest decreases in ozone and that the decreases occur at the times of greatest concentration. More rural and high elevation sites show a stronger spring maxima. Sites at high altitude show the weakest diel cycles.

temperatures have gone down while summer and fall temperatures have gone up.

The estimates for each time of a day h for each of the plots in Figs. 2–5 are computed separately. When we put the hourly, calculated values all together we reconstruct the full diel cycle. The reconstructed diel and seasonal variation look realistic, with maximal temperatures in summer afternoons and minimal temperatures in the early morning hours of winter, and this gives us some assurance that the method applied here appropriately represents cycles of the tropospheric ozone and temperature.

5. Discussion

For the most polluted sites Beltsville, MD (located between Washington, DC and Baltimore, MD) and Penn State, PA (located downwind of the heavily industrialized Ohio River Valley) average surface rural ozone mixing ratios follow known annual and diel

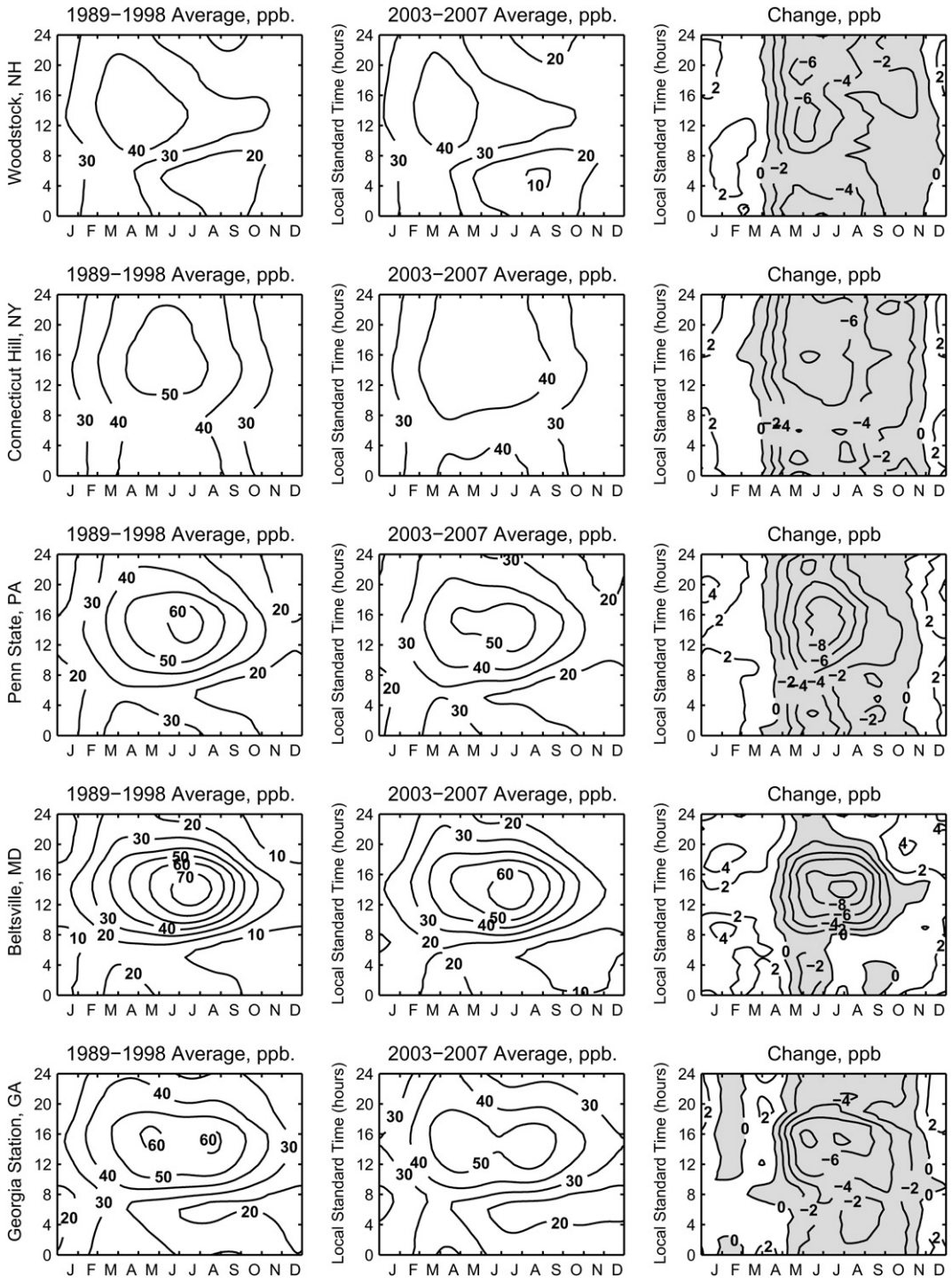

Fig. 3. Diel and Seasonal distribution of observed ozone concentrations at five rural monitoring stations across the eastern U.S. of the CASTNET network for the period 1989–1998, before a 43% average NOx reduction at power plants, and for the period 2003–2007, afterwards. Decreases and negative values are shaded.

cycles (Figs. 2 and 3), going from highest during summertime afternoon hours to lowest in winter just before dawn. These sites show the strongest diel cycles as well, reflecting the dominant role played by photochemical production during the day and loss by titration (or sequestration in reservoir species) at night. Maxima in surface ozone amounts occur simultaneously with the maxima in surface air temperatures in the afternoon of late summer months. The diel variation indicates that the maxima of both surface ozone and temperature occur shortly after the maxima of incoming solar radiation (Figs. 4 and 5). This is not the time of greatest heating, but the latest time of day when heating exceeds cooling. Likewise ozone maxima are observed at the latest time of the day when production exceeds loss.

Georgia Station, GA, a less polluted site at 270 m above sea level, shows a broader maximum extending into spring. This reflects the combination of regional photochemical ozone production and large-scale transport from the upper troposphere/lower stratosphere. High altitude sites can be above the planetary boundary layer,

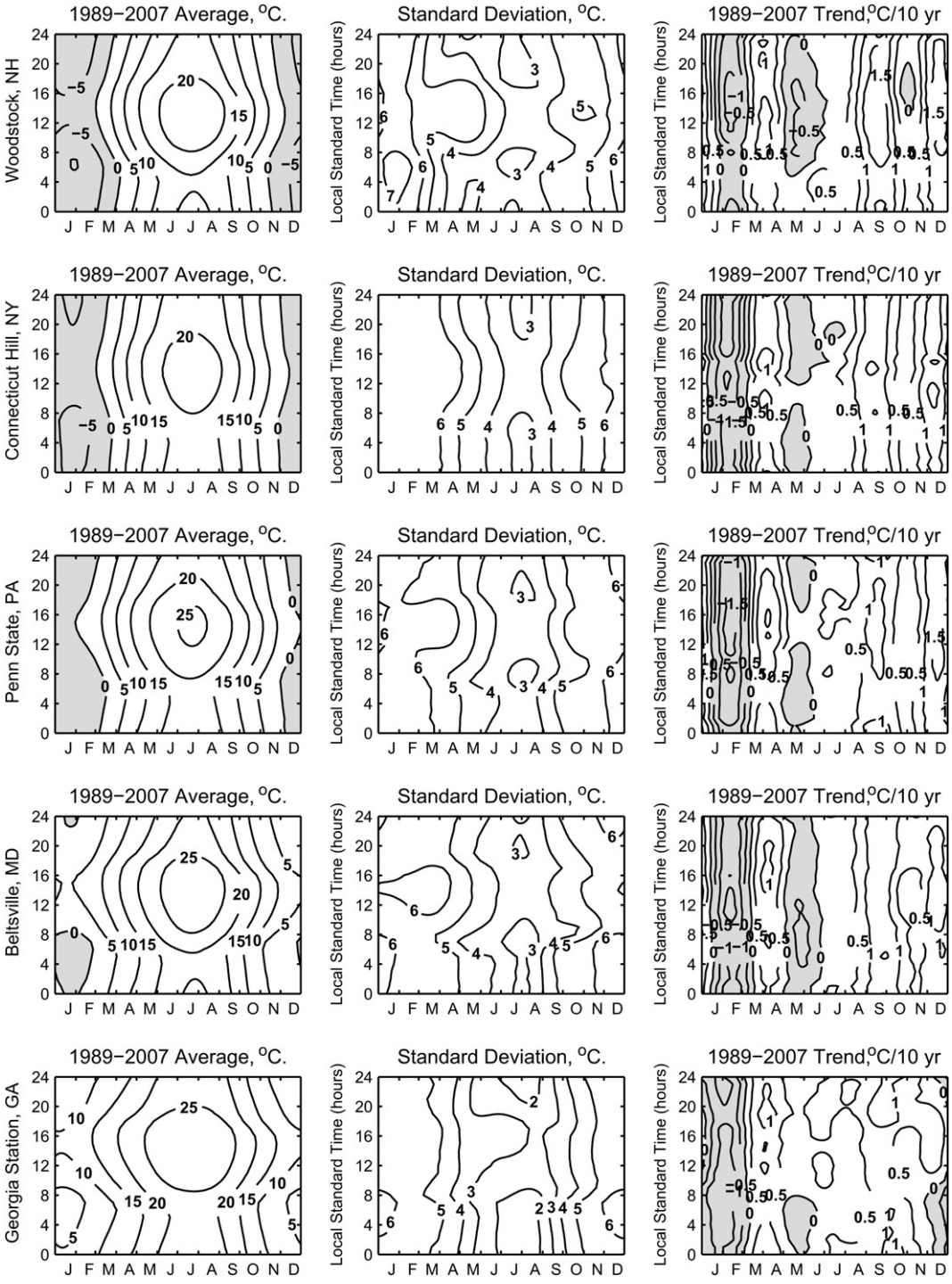

Fig. 4. Diel and Seasonal distribution of 1989–2007 means, standard deviations and linear trends of observed surface air temperature at five CASTNET stations. Decreases and negative values are shaded.

especially at night, and show weaker diel cycles. The two most northerly sites, Connecticut Hill, NY and Woodstock, NH, (both at relatively high altitude; see Table 1) show more distinct mid to late spring maxima. For these sites the daily ozone maxima occur at the time of daily temperature maxima, but the seasonal ozone maxima occur earlier than the seasonal temperature maxima. The relative importance of stratospheric ozone and ozone resulting from the decomposition of NOx reservoirs such as PAN is greater at these more rural and more northerly sites.

Looking at Fig. 2, the overall trend in ozone, displayed in the column on the right, is decreasing concentrations at all the stations in the summer months. Decreases are most pronounced in months with the highest readings at all stations. The stations with the highest values, and the more suburban location, show the largest decreases, the strongest diel cycle, and the largest decreases occurring at hours (and months) with the highest concentrations. For example the Beltsville, MD station shows 6 ppbv decade^{-1} decreasing trend in July and August ozone from about noon to 4 pm.

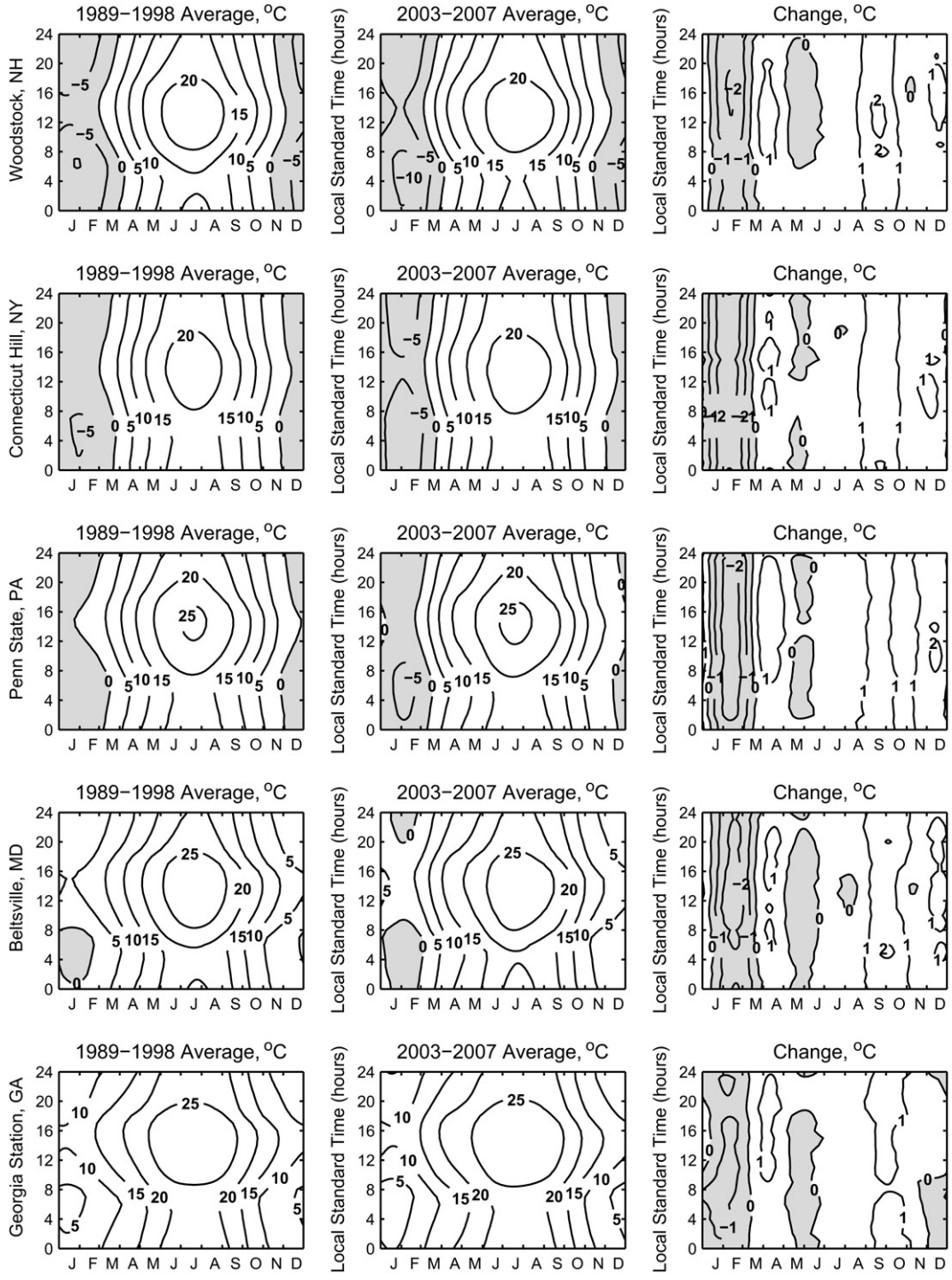

Fig. 5. Diel and Seasonal distribution of observed surface temperatures at five CASTNET stations for the period 1989–1998, before a 43% average NOx reduction at power plants, and for the period 2003–2007, afterwards. Decreases and negative values are shaded. In general decreases are seen for the winter and spring and increases for summer and fall.

This coincides with a much larger decrease across the 2002 emission change as shown in Fig. 3. The diel cycle in the trend is weaker at the more rural stations of Woodstock and Connecticut Hill, but the decreasing summertime trend is evident across the Eastern US from NH to GA. This is strong evidence for the effective implementation of power plant NOx emission controls decreasing regional, rural, surface ozone amounts.

The decreasing trend in ozone amounts is largest during the period of highest values and greatest variability. This time period is of greatest concern to policy makers. The exposure and environmental damage associated with the worst effects of tropospheric ozone air pollution occur during the summer months and in the afternoon. The accumulated exposure over years to decades leads to large-scale damage to crops and important plant species such as sugar maple and apple orchards (U.S. EPA, 2006). A declining trend is therefore of great ecological and economic significance.

The collocation of temperature and ozone data allows interesting insight although the data record is not long enough to make

conclusions regarding climatic scale trends. Fig. 4 indicates noticeable increasing temperatures in the summer and fall across the rural eastern United States. Increasing temperature trends from a half to one degree per decade occur across all five sites from June through the end of the year. Additional temperature increases, from half to one degree per decade, are observed in the spring months of March and April. The temperatures in the winter months of January and February appear to decline with a trend of about 1 °C per decade in afternoon temperatures in January and early February. Average temperatures reflect the strong, mid-latitude annual cycle with highest temperatures occurring in the afternoon of the summer months. Eastern US is fairly consistent with average summertime afternoon temperatures in excess of 20 °C with longer periods of higher temperatures in the South (GA) and slightly shorter periods in MD into PA and continuing to decrease at further sites to the North (NY and NH.) The variation in these data is relatively small with about 4 °C standard deviation the largest and occurring in the boundary from summer to winter. There is no significant diel signal to these trends as can be seen in the right panels. (vertical patterns are relatively constant across the day.)

Looking back at Fig. 2, there are times with increasing surface ozone including the winter months of December, January and February and early spring of March and April and extending into May at the southernmost site. This could be taken as an indication that pollution control strategies need to be reconsidered where a strong weather signal, as represented by temperature here, occurs. Some hypotheses to investigate include potential decreasing amounts of NO resulting in less O_3 titration, or increased stratospheric intrusion, or greater lightning activity leading to more O_3, but these small increases are a relatively minor concern for air pollution policy considerations at this time. Due to the overall low values and relatively small amount of exposure associated with these rural locations consideration should be made regarding the impact upon higher concentrations, more populated regions, and how this rural signal informs policies such as the length of the regulatory ozone season.

The tendency seen in the temperature data described above combined with the known correlation of higher ozone amounts to higher temperatures (Bloomer et al., 2009; Weaver et al., 2009), and with consideration of existing modeling study results projecting higher ozone amounts in future years with higher temperatures when emissions are held constant (Jacob and Winner, 2009), indicates additional observations and study are warranted to assess: the length of the regulatory ozone season, whether or not it may need to be extended, and to document the impact of changing climate as conditions continue to change in response to warming or as policies are implemented to lower the threshold values for the National Ambient Air Quality Standard.

6. Conclusions

Some specific conclusions arise from careful examination of the data presented here as a result of the application of a new method of air quality trend analysis. These include:

1. During the past two decades, ozone concentrations have been, in general, decreasing as seen in both the linear trend analysis and when comparing averages before and after a large reduction in power plant NOx emissions during the existing regulatory ozone season. Rural surface ozone amounts decreased up to 6 ppb decade^{-1} and decreased across the emission reduction threshold of 2002 by 6–10 ppb. Results are consistent across the entire rural eastern US as sampled by the five sites analyzed and presented here.
2. The greatest downward trends in pollution ozone occur at the locations and times of greatest smog – in the summer months, during the afternoon, at the most polluted sites. This presents strong evidence that the implementation of power plant NOx emission controls have decreased regional, rural, surface ozone amounts when and where improvements are most needed.
3. The winter months and early spring show increasing ozone amounts. This may result from decreased NO titration or other effects and warrants further investigation.
4. Ozone Maxima in the early spring at the high-latitude stations with significant elevation above sea level indicate stratospheric intrusions and widely-spread, long-lived pollutants acting as reservoir species for ozone formation are a relatively strong source of ozone to these stations. The absence of a daily temporal trend and the absence of significant differences before and after the US stationary source emission reductions support this conclusion for the spring months.
5. There is evidence (Fig. 3) that daytime values are higher in the early spring than they were before 2002. This may be the result of local climate change since it coincides with warming trends (Fig. 4) and warmer temperatures (Fig. 5) and suggests the possibility that the ozone season is getting longer and is worthy of further research.
6. Summer temperatures are warming during the times of ozone decreases in our analysis. But, it is well known that ozone generally increases with warming air temperatures. This is additional proof that emission reductions, and not changes in weather or climate, are responsible for the observed, decreasing, ozone trends.

Overall, ozone is trending downward at the hours and during the months of highest values that are of greatest concern to air quality planners and affected, at-risk, populations. This is in contrast to concurrent warming temperatures. Given the phenomenological shift of precursor emissions at power plants our analysis provides strong evidence that these emission reductions are effective at lowering regional ozone amounts. The method presented here provides a tool for investigating long-term trends in ozone and temperature useful to air quality planners and scientists interested in climate change and the effects on ozone air quality.

Acknowledgments

BJB was supported by US EPA. RRD and KYV were supported by Maryland Department of the Environment. The authors thank Nickolay Krotkov and an anonymous reviewer for constructive comments and insightful questions. Statements in this publication reflect the authors' professional views and opinions and should not be construed to represent any determination or policy of the US EPA.

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