Increasing background ozone in surface air over the United States

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Abstract. The long-term trend of background O_3 in surface air over the United States from 1980 to 1998 is examined using monthly probability distributions of daily maximum 8-hour average O_3 concentrations at a large ensemble of rural sites. Ozone concentrations have decreased at the high end of the probability distribution (reflecting emission controls) but have increased at the low end. The cross-over takes place between the 30th and 50th percentiles in May-August and between the 60th and 90th percentiles during the rest of the year. The increase is statistically significant at a 5% level in spring and fall, when it is 3-5 ppbv. The maximum increase is in the Northeast. A possible explanation is an increase in the O_3 background transported from outside the United States. Better understanding of the causes of the increase is needed because of its implications for meeting O_3 air quality standards.

Introduction

Ozone in surface air is produced by photochemical oxidation of hydrocarbons and CO in the presence of nitrogen oxides ($NO_x = NO + NO_2$). High anthropogenic emissions of NO_x and hydrocarbons in populated regions of the United States result in surface O_3 concentrations that exceed air quality standards. As of 1998, 51 million persons in the United States lived in areas failing to meet the current O_3 standard (120 ppbv, 1-hour average), and 130 million persons lived in areas where O_3 levels exceed the new proposed standard (80 ppbv, 8-hour average) [*U.S. Environmental Protection Agency (EPA)*, 2000]. It is estimated that anthropogenic emissions of hydrocarbons in the United States decreased by 30% from 1980 to 1998, while NO_x emissions remained constant within a few percent [*EPA*, 1998, 2000]. Hydrocarbon emission controls are credited for abating the most extreme O_3 pollution events, but decreases in less extreme statistics of O_3 concentrations have been far less conclusive, leading to concern over the achievability of the new standard [*Lefohn et al.*, 1998].

Altshuller and Lefohn [1996] point out that an important consideration for pollution control strategies is the O_3 background present in surface air over the United States. They define this background as the O_3 concentration that would prevail in the absence of domestic anthropogenic emissions. They discuss different ways by which it may be estimated including measurements at clean sites, analysis of the probability distribution of O_3 concentrations, and correlations with reactive nitrogen oxides (NO_y, including NO_x and its

oxidation products). By examining results from these different approaches they estimate a background daytime concentration of 35 ± 10 ppbv in summer, amounting to almost half of the new air quality standard. Although *Altshuller and Lefohn* [1996] view this background as natural, there is in fact good evidence that it includes a major anthropogenic component associated with intercontinental transport of pollution [*Marenco et al.*, 1994; *Wang and Jacob*, 1998]. The lifetime of O_3 in the free troposphere is sufficiently long (several weeks) that anthropogenic O_3 pollution can circumnavigate the globe and enhance O_3 over the entire northern midlatitudes belt [*Logan*, 1985].

We examine here the long-term trend in the O_3 background in surface air over the United States from 1980 to 1998 by analyzing the probability distribution of O_3 concentrations at rural sites. A trend in the background could have important implications for meeting O_3 air quality standards. *Jacob et al.* [1999] projected that industrialization of eastern Asia would increase mean surface O_3 concentrations over the United States by 2–6 ppbv over the 1985–2010 period, significantly offsetting the benefits of domestic emission controls. Observations at Whiteface Mountain (1480 m) in New York State indicate an increase of 4 ± 2 ppbv over the period 1974–1995 [*Oltmans et al.*, 1998]. Ozonesonde data in the free troposphere at Wallops Island (Virginia) and Boulder (Colorado) show no significant increase over the past two decades but the data are sparse [*Oltmans et al.*, 1998; *Logan et al.*, 1999].

Methods

We use the 1980–1998 database of hourly O_3 observations compiled by the EPA Aerometric Information Retrieval System (AIRS). This database includes over 2000 sites in the contiguous United States, though many have limited records. The sites are classified in the database as urban, suburban, or rural. We examine the change over the 19-year period in the probability distribution of the daily maximum 8-hour average O_3 concentration at rural sites, for each month of the year. The probability distributions are constructed by aggregating data for all rural sites in the contiguous United States that have at least 16 days of data for the relevant month and for each year used in the analysis. The daily maximum 8-hour average concentration on a given day and at a given site represents one point in the probability distribution, and we collect the ensemble of points for all days and for all sites to generate the full probability distribution.

We compare the probability distributions for the two ends of the record, 1980–1984 vs. 1994–1998; there are 19–59 rural sites satisfying the data selection criterion (at least 16 days of data per month for each of the 10 years) depending
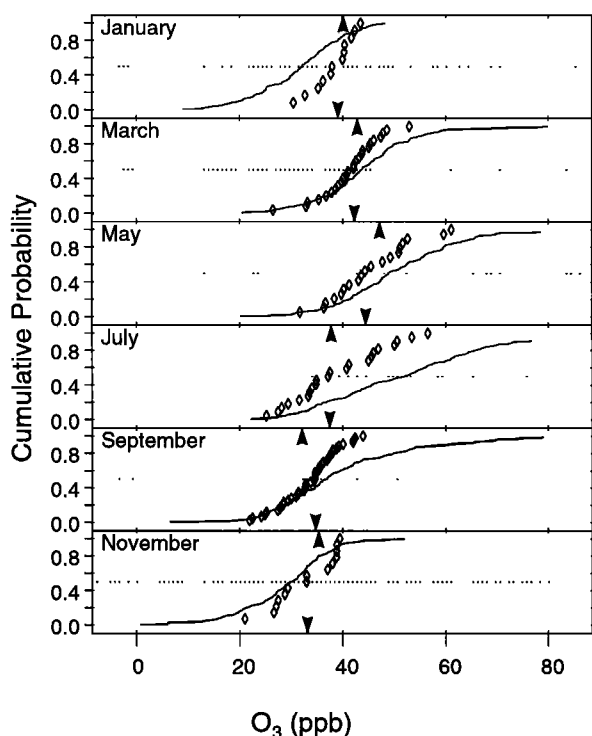
Figure 1. Monthly cumulative probability distributions of the daily maximum 8- hour average O_3 concentrations at Harvard Forest in central Massachusetts in 1990–1998. The solid line is for the ensemble of data and the diamonds are for the subset with NO_y concentrations below the monthly median. Also shown are the background O_3 concentrations estimated as the median values for the subsets of data with CO or NO_y concentrations below their 25th percentiles for the month (arrows on the top and bottom axes, respectively).

on the month. Consideration of 5-year periods reduces the effect of interannual variability associated with meteorology. Inspection of the 1980–1998 time series shows that the 1980–1984 and 1994–1998 segments include no particularly anomalous year and capture a typical range of interannual variability [*Lin*, 2000]. As an independent second approach we also conduct linear regressions on time of the 10th, 20th, and 30th percentiles of the probability distribution, using data for all 19 years of the 1980–1998 record. There are 16–55 sites satisfying the data density criterion for the linear regression analysis depending on the month, less than in the first approach which requires only 10 years (1980–1984 and 1994–1998) instead of 19 years.

Relating the O_3 probability distribution to the background O_3 concentration is not straightforward. One approach for estimating the background is by correlation with low concentrations of NO_y or CO [*Trainer et al.*, 1993; *Altshuller and Lefohn*, 1996]. The AIRS sites do not have data for NO_y or CO with the sensitivity needed for such an analysis. One rural site where year-round, high-quality measurements for NO_y and CO concentrations are available starting in 1990 is Harvard Forest in central Massachusetts [*Munger et al.*, 1996]. Figure 1 (solid lines) shows the monthly probability distributions of daily maximum 8-hour average O_3 concentrations at that site. Arrows indicate the background O_3 concentrations estimated as the median values for the lowest 25th percentiles of CO and NO_y concentrations.

These background concentrations range from 35 ppbv in the fall to 45 ppbv in early spring, consistent with the analysis of *Altshuller and Lefohn* [1996].

We see from Figure 1 that the O_3 background at Harvard Forest, as estimated above, corresponds to the 25th percentile of the O_3 probability distribution in summer, the 80th in winter, and the 50th in spring and fall. Such seasonal variation is consistent with observations of the O_3:CO relationship in maritime Canada downwind of the United States, which show that U.S. pollution is strongly enriched in O_3 relative to background during May-September but not during the rest of the year [*Parrish et al.*, 1998]. Thus, except in winter, we may view the lower half of the probability distribution as containing a strong background influence. Percentiles below the estimated background in Figure 1 presumably reflect O_3 depletion from deposition, although titration by fresh emissions of NO must also be considered. The latter effect is most important in winter, when NO_x emissions in the United States consume rather than produce O_3.

Titration by NO could be a problem when interpreting long-term trends in the lower end of the O_3 probability distribution as trends in background O_3 concentrations. We minimize this effect in our analysis in two ways. First, by considering the daily maximum 8-hour average concentration we effectively exclude nighttime periods when titration is most important [*Logan*, 1989]. Second, we limit our attention to sites classified by AIRS as rural (*Fiore et al.* [1998] have previously shown a good correspondence between the AIRS rural classification and low NO_x emissions). Titration should have little effect on O_3 at rural sites outside of winter, since NO_x concentrations there are generally less than 3 ppbv [*Parrish et al.*, 1993; *Munger et al.*, 1996]. Figure 1 shows the O_3 probability distributions at Harvard Forest for the subset of data with NO_y concentrations below the median (diamonds); a titration effect at the low end of the distribution is evident in winter (January) but not in other seasons.

Results and Discussion

Figure 2 compares the 1980–1984 and 1994–1998 cumulative probability distributions of O_3 concentrations at the en-
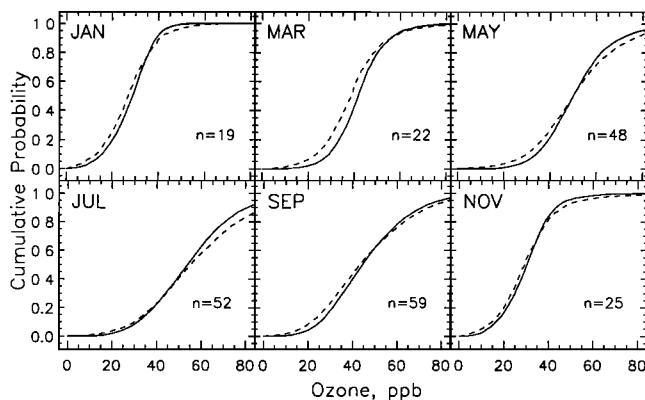
Figure 2. Cumulative probability distributions of the daily maximum 8-hour average O_3 concentrations at rural sites in the United States in 1980–1984 (dashed line) and 1994–1998 (solid line). See text for details.

semble of rural sites in the United States. All months show the same qualitative trend of decreasing concentrations at the high end of the probability distribution and increasing concentrations at the low end. The cross-over takes place in the 30–50th percentile range in May-August and in the 60–90th percentile range during the rest of the year, reflecting the faster local production of O_3 from domestic emissions in summer. The O_3 concentration at the crossover point is 45–55 ppbv in March-October and 35–40 ppbv in November-February.

The decreasing trend at the high end of the probability distribution has been noted before [Fiore et al., 1998; Lefohn et al., 1998; EPA, 2000]. We focus our attention on the increasing trend at the low end. The increase is largest in spring, when concentrations up to the 50th percentile show an increase of 3–5 ppbv. We examined the statistical significance of the increase by comparing the populations of 10th, 20th, and 30th percentiles between the two 5-year periods. This was done as follows. For each month and for each year the relevant percentile of the daily maximum 8-hour average concentration at each site was calculated. The values compiled in this manner for all sites were then separated into two samples, one for 1980–1984 and the other for 1994–1998, and a two-sided t-test was conducted to assess the significance of the difference between the means of these two samples. We find that the increases for these three percentiles are statistically significant at a 5% level in March through May and in September-October.

As an alternate approach to trend analysis we also used linear regressions on time of the 10th, 20th, and 30th percentiles, using data for all 19 years of the 1980–1998 record. For each month and for each year we calculated the relevant percentile of the daily maximum 8-hour average O_3 concentration at each site, took the average of the resulting values over all sites for that month and year, and performed linear regressions on time for individual months. Results are presented by Lin [2000]. For the 10th and 20th percentiles, we find increasing trends that are significant at the 5% level in March through May and in September-October. For the 30th percentiles, the increasing trends are significant only in March and October. Note that trends are not necessarily linear, and our first approach based on comparison of the two 5-year segments makes no assumption as to linearity.

Lefohn et al. [1998] previously noted an increase in the low end of the probability distribution of O_3 concentrations at four sites in the United States in 1980–1995, and attributed it to a decrease in NO emissions resulting in less effective titration. As pointed out in the previous section, it is unlikely that this effect could be significant in our analysis. In order to check that a decrease in the effectiveness of titration by NO was not responsible for our observed increases in the low end of the O_3 probability distribution, we examined the 1980–1998 trends for the ensemble of urban sites in the AIRS database, using the same procedures as above. Although titration is far more important at urban than at rural sites, probability distributions for urban sites reveal similar or even smaller increases at the low end, demonstrating that the increases in rural areas are due to factors other than titration by NO. Our result for urban sites is not surprising, considering that estimated NO_x emissions nationwide show no trend over the 1980-1998 period [EPA, 1998, 2000].

The observed increase in the low end of the O_3 probability distribution could be due to an increase in the back-

ground O_3 pollution transported from outside the United States. The maximum increase in spring, and to a lesser degree in fall, is consistent with more effective circumpolar transport of O_3 pollution at northern midlatitudes in that season due to a combination of relatively efficient O_3 production, strong circulation, and long O_3 lifetime [Wang et al., 1998]. Other explanations seem less satisfactory. Gradual suburbanization of rural sites could lead to an increase in O_3 but the effect would be felt over the whole probability distribution. An increase in local vehicle traffic (NO emissions) associated with suburbanization would actually cause a decrease in the low end of the O_3 probability distribution due to titration. Trends in forest fires in Canada could affect O_3 concentrations [Wotawa and Trainer, 2000] but the effect would be mainly in summer. Increased injection of O_3 from the stratosphere is unlikely considering that O_3 concentrations in the lower stratosphere have decreased during the past two decades; tropospheric O_3 concentrations measured from ozonesondes in Canada decreased by 2–8% per decade over the period 1980–1996, suggesting a decrease in the supply of O_3 from the stratosphere [Logan et al., 1999].

We examined the geographical distribution of the trends in the O_3 probability distribution for 1980–1998 by partitioning the United States into four quadrants at 36°N, 97.5°W. Asian industrialization would have the greatest effect in the western United States in spring [Jacob et al., 1999; Jaffe et al., 1999]. We find that the trends are qualitatively the same in all quadrants but are largest in the Northeast, a result which is not consistent with Asian influence. The paucity of sites in the western United States (6–13 sites depending on the month) may hinder detection of an Asian signal. Continued observations of trends are needed. Global three-dimensional model analyses may help to determine if changes in emissions of O_3 precursors at northern midlatitudes or other factors, such as depletion of stratospheric O_3 allowing increased UV penetration in the troposphere, can account for the observed trends.

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