TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **54**:681–688

Ozone and Other Air Quality-Related Variables Affecting Visibility in the Southeast United States

Viney P. Aneja, Jeffrey S. Brittig, and Deug-Soo Kim
Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina

Adel Hanna
Carolina Environmental Program, University of North Carolina, Chapel Hill, North Carolina

ABSTRACT
An analysis of ozone (O_3) concentrations and several other air quality-related variables was performed to elucidate their relationship with visibility at five urban and semi-urban locations in the southeast United States during the summer seasons of 1980–1996. The role and impact of O_3 on aerosols was investigated to ascertain a relationship with visibility. Regional trend analysis over the 1980s reveals an increase in maximum O_3 concentration coupled with a decrease in visibility. However, a similar analysis for the 1990s shows a leveling-off of both O_3 and visibility; in both cases, the results were not statistically significant at the 5% level. A case study of site-specific trends at Nashville, TN, followed similar trends. To better understand the relationships between O_3 concentration and visibility, the analysis was varied from yearly through daily to hourly averaged values. This increased temporal resolution showed a statistically significant inverse relationship between visibility and O_3. Site-specific hourly r^2 values ranged from 0.02 to 0.43. Additionally, by performing back-trajectory analysis, it was found that the visibility degraded by air mass migration over polluted areas.

INTRODUCTION
Visual air quality (VAQ) has become a major concern not only in pristine areas such as national forests[1] but in urban environments as well.[2] Good VAQ improves peoples' daily lives and improves many recreational opportunities, such as the enjoyment of national parks and monuments. When visibility is reduced by airborne pollution, the human eye perceives a loss in color, contrast, and detail; objects no longer appear crisp and clear.[3]

In 1952, Haagen-Smit first used the term "photochemical smog" to describe the mix of air pollutants that arise in the Los Angeles area as a result of the oxidation of volatile organic compounds (VOCs) or nonmethane hydrocarbons and nitrogen oxides (NO_x) in the presence of sunlight and water vapor. Tropospheric ozone (O_3) is a product of this photochemical process. O_3, an oxidant itself, generates hydroxyl radicals (OH), which in turn influence the concentration of trace gases and the production of fine particles (aerosols), which reduces visibility. O_3 and fine particulate matter (PM) are chemically coupled.[5] However, meteorological processes may influence this coupling.

Visibility reduction is caused largely by the presence of secondary fine aerosol particles (produced by gas-to-particle conversion), whose production depends on the oxidizing capacity of the atmosphere. The rate of this oxidation is dependent on the availability of free radicals and other oxidants such as O_3, hydrogen peroxide, and nitric acid (HNO_3). O_3 is important because of its abundance, oxidizing capacity, and ability to produce free radicals.

Reductions in visibility occur when particles, and to a lesser extent gases, scatter or absorb light; this process is known as light extinction. Fine aerosol particles (i.e., between 0.1 and 1 μm in diameter) are most effective on a per-mass basis in reducing visibility.[6] Visibility can be associated indirectly to atmospheric loading (the amount of PM) through the use of Koschmeider's equation, which relates visual range to light extinction. Regional-scale haze in the eastern United States is dominated by sulfates.[7] Chemical analysis reveals that 40–70% of the fine

IMPLICATIONS
The climatological (1980–1996) analysis of O_3, aerosol, and other air quality-related variables provides an opportunity to study the response of visibility to their changes. The changes in visibility associated with benefits from the 1990 Clean Air Act Amendments may be ascertained from this temporal analysis of air quality. This will provide policy-makers and regulators with an observational and modeling-based tool to improve regional visibility.

particle mass over the eastern United States is composed of sulfates, associated with ammonium ion (NH_4^+) and water.[8,9] It is therefore hypothesized that the O_3 produced in a polluted environment reacts to produce free radicals—in addition to its oxidizing capacity—which increase the oxidizing capacity of the atmosphere and help to convert primary precursor pollutants (i.e., sulfur dioxide; SO_2) into visibility-reducing fine particles (i.e., sulfate; SO_4^{2-}).[10] Because of their size, sulfates are a major contributor to light extinction and visibility degradation.[11] This reduction of horizontal visibility caused by atmospheric aerosols has been suggested as a possible indicator and method for monitoring pollution. Further analysis has been recommended on the relationship between O_3 and air quality variables (such as visibility) for summertime pollution episodes.[12]

METHODOLOGY

In this work, nine sites in five different metropolitan areas throughout the southeast United States were analyzed for O_3 and meteorological trends during a 17-year period (1980–1996). It has been found that O_3 correspondence to meteorological parameters in the southeast United States is best established during the summer months from June to August and between the daytime hours 1000 and 1600 local, the peak solar heating hours.[13] An "O_3 season" was therefore defined as the months of June, July, and August and included observations from 1000 to 1600 local. The data utilized for this study, thus, adopted these same time constraints during those observational periods (17 years).

Hourly averaged O_3 and meteorological data were obtained from the U.S. Environmental Protection Agency's Aerometric Information Retrieval System (EPA-AIRS) database and the Air Force Combat Climatology Center (AFCCC) database at Scott Air Force Base, IL, respectively. Once the data had been retrieved, they were processed and reduced for analysis by utilizing the statistical software package, SAS. Monthly and annual averages for each site were produced by SAS proc Means procedure, and, averaged together, these sites constitute the regional data. Visual range (*R* [v]) was measured by both human observation and an automated system. The automated instrument-derived visibility observation is a sensor value converted to an appropriate visibility value using algorithms representative of the prevailing visibility.[14] The commissions of these automated systems occurred during the last 2 years at all the study sites except Charlotte, NC. Visual range related to haze situations is better measured at around local noon when the relative humidity is $<70\%$. Because certain transient weather is known to cleanse both visibility-reducing fine particles and O_3 from the atmosphere, hourly observations containing any form of precipitation were removed from this analysis. However, fog was not included in this precipitation removal process, because the occurrence of fog was not expected to be a factor after 10:00 a.m. local time. The most noticeable consequence of this data removal during precipitation was that data for higher relative humidity ($>95\%$), generally associated with precipitation, were removed. In addition, $PM_{2.5}$ mass, as a surrogate for visibility, correlates with ambient maximum hourly O_3 and exhibits a seasonal pattern. During the warm months (May–September), stronger correlation between $PM_{2.5}$ and the maximum hourly O_3 was observed than during the cold months.[9] In this work, our analysis is confined to the daytime hours of 1000 to 1600 local time of the summer months, June–August, for the 17-year period.

Statistical significance was determined by hypothesis testing (i.e., H_0: slope = 0, H_1: slope $\neq$ 0) utilizing an appropriate distribution and test statistic. Two-tailed significance probabilities less than 0.05 (α = 0.05) were considered to be statistically significant.

RESULTS AND DISCUSSION

Figure 1 shows O_3 trends for the nine sites used in this study. The figure reveals a general decline of O_3 concentrations during the 1990s compared with the 1980s. This result agrees with the analysis of $PM_{2.5}$ concentrations based on measurement campaigns.[9] Similar declines in PM_{10} also were noted by EPA.[3] For the region as a whole, O_3 trends (see Figure 2) show that the average daily maximum O_3 concentrations have leveled off during the 1990s (−0.00007 ppmv/yr, r^2 = 0.0007) compared with the steady increase during the 1980s (0.0005 ppmv/yr, r^2 = 0.0497). While these results may be explained as a result of the 1990 Clean Air Act Amendment (CAAA) regulations, it must be noted that O_3 formation is a highly complex, nonlinear reaction.[15] Year-to-year fluctuations in meteorology can easily mask and confuse its relationship with O_3. In that case, trends in ambient O_3 concentrations do not necessarily indicate that O_3 control strategies are attaining the desired result because variation in the meteorological conditions may significantly affect the observed trend.[13,16–18]

Regional Yearly Anomalies

Averages of O_3, visibility, relative humidity, and temperature were calculated for the entire 17-year period and then subjectively compared against yearly means of each variable (see Figure 3). The results then were plotted on a bar graph to highlight anomalies by year. Inverse relationship of O_3 (see Figure 3a) with relative humidity (see Figure 3b) was evident in nearly all years (94% of the time). Likewise, the direct relationship between O_3 and temperature (see Figure 3c) was clearly evident, except for 1991.

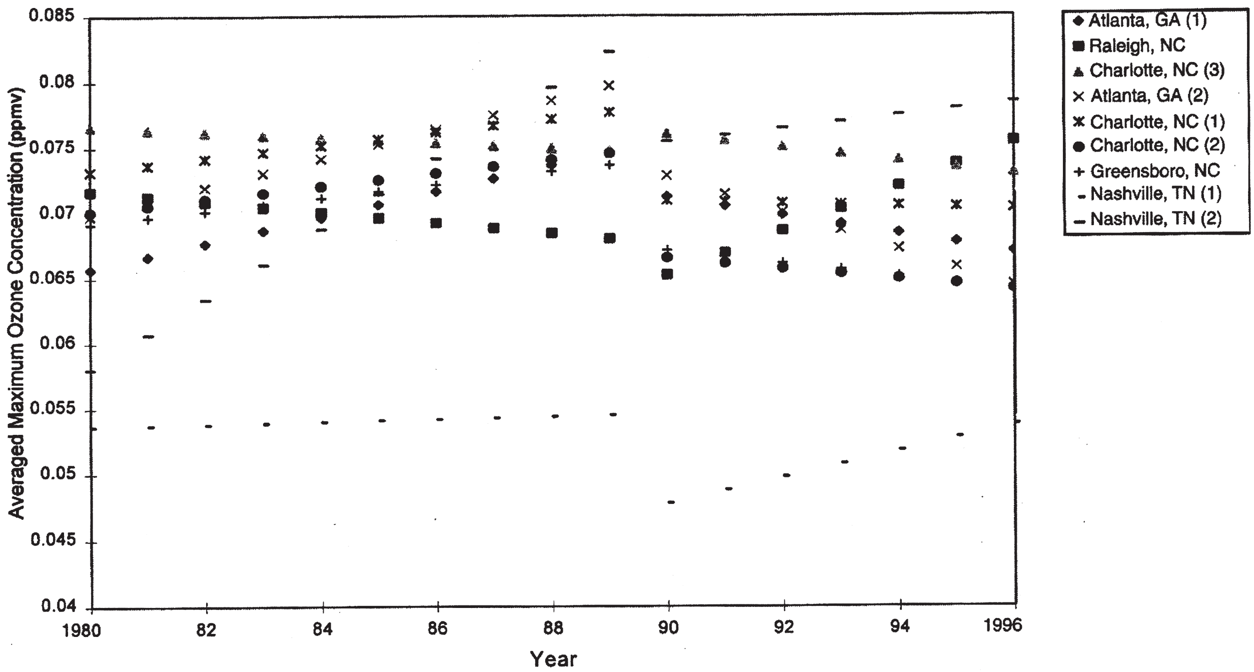

Figure 1. Individual O_3 trends for each site, collectively used to construct the regional trend.

A consistent relationship between visibility (see Figure 3d) and the other variables is not clearly evident in the anomaly analysis. Only 8 of the 17 years (47%) show an inverse relationship between O_3 and visibility. Nine of the years (53%) showed a positive relationship between relative humidity and visibility, while nine of the years (53%) revealed an inverse relationship between temperature and visibility. To further analyze these results, temporal resolution was increased at a specific site as a case study.

Nashville Case Study

A site-specific data analysis for Nashville, TN (latitude 35.9° N, longitude 86.8° W), was conducted utilizing yearly, daily, and hourly summaries. First, a regression

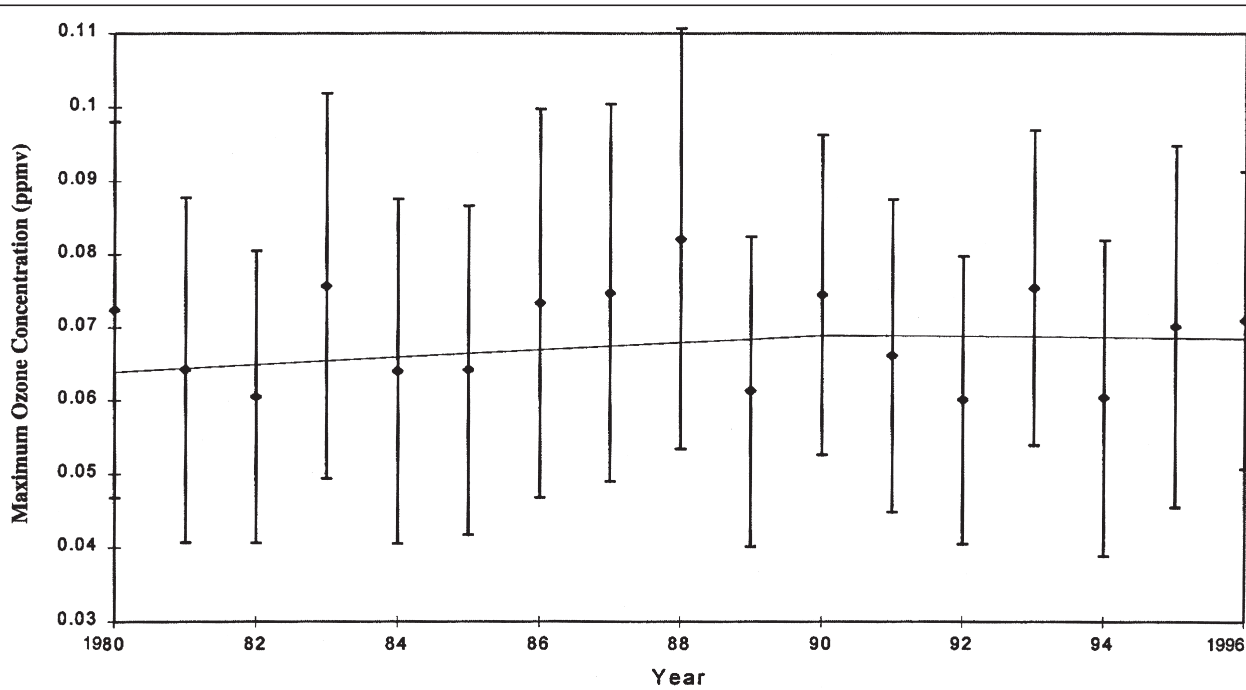

Figure 2. The overall regional southeast United States O_3 trend 1980–1996.

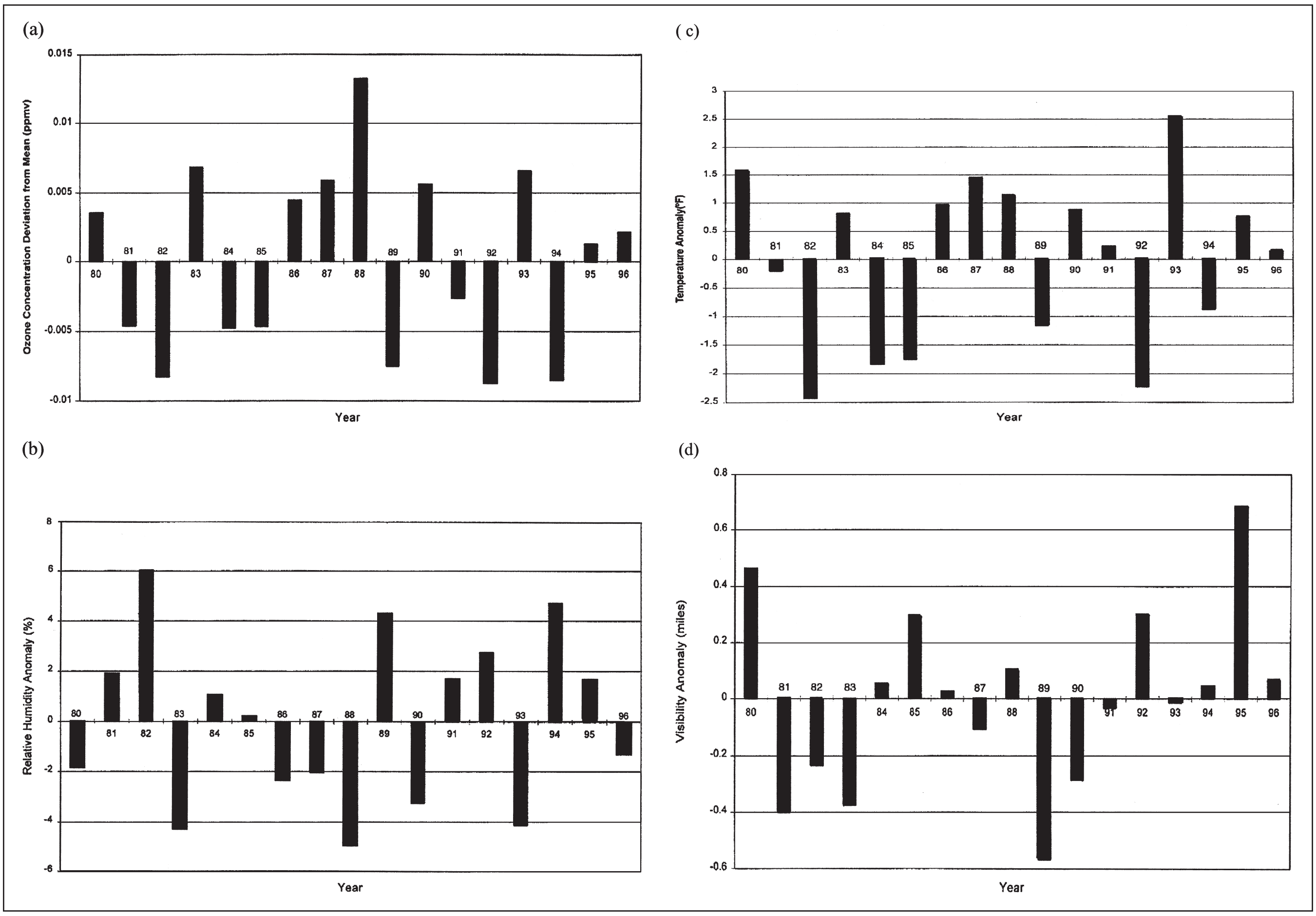

Figure 3. (a) Regional yearly averaged O_3 anomalies; (b) Regional yearly averaged relative humidity anomalies; (c) Regional yearly averaged daily maximum temperature anomalies; (d) Regional yearly averaged visibility anomalies.

analysis was performed utilizing all Nashville hourly observations during the 17-year period of the analysis. Although a statistically significant inverse relationship emerged between visibility and O_3 (p value = 0.0001), the data were very noisy; hence, a low r^2 of 0.01 was observed (see Figure 4).

Nashville Yearly Trends

O_3 trend analysis in Nashville (see Figure 5) shows the averaged yearly visibility and their trends were positive in the 1980s (0.0013 ppmv/yr, r^2 = 0.2244), and unlike the region as a whole, which leveled off during the 1990s, O_3 continued to increase during the same period (0.0009 ppmv/yr, r^2 = 0.0849). The visibility trend of Nashville (see Figure 5) for the 1980s decreased (−0.902 mi/yr, r^2 = 0.108), consistent with the rising O_3 trend during the same period, clearly showing an inverse relationship. However, the inverse relationship is not pronounced during the 1990s (0.0139 mi/yr, r^2 = 0.0034). Temperature trends at Nashville were slightly positive during the 1980s (0.0387 °F/yr, r^2 = 0.0035) and negative for the 1990s (−0.3616 °F/yr, r^2 = 0.147). Relative humidity trends displayed a slightly negative slope for the 1980s (−13.79%/yr, r^2 = 0.009) and a relatively steep positive slope during the 1990s (109.8%/yr, r^2 = 0.3215). As previously mentioned, none of the trend analysis presented proved to be significant at or below the 5% level of significance; however, the variances appeared to be constant over time.

Nashville Yearly Anomalies

Eight of the 17 years showed an inverse relationship between O_3 and visibility. Of those years not fitting this relationship, the relative humidity anomalies were significantly different from the normal mean (over the 17-year data period), suggesting a strong influence of moisture on visibility, unlike that seen in the regional trend analysis.

Anomalies of temperature and O_3 did not indicate a direct relationship for all years as it had in the regional analysis. This suggests that regional transport of O_3 and its precursors may play an important role in local ambient O_3 concentrations. Furthermore, there were large standard deviations with the yearly averaged data, especially with visibility, whose temporal variation is best evaluated on an hourly or daily—not a yearly—basis.

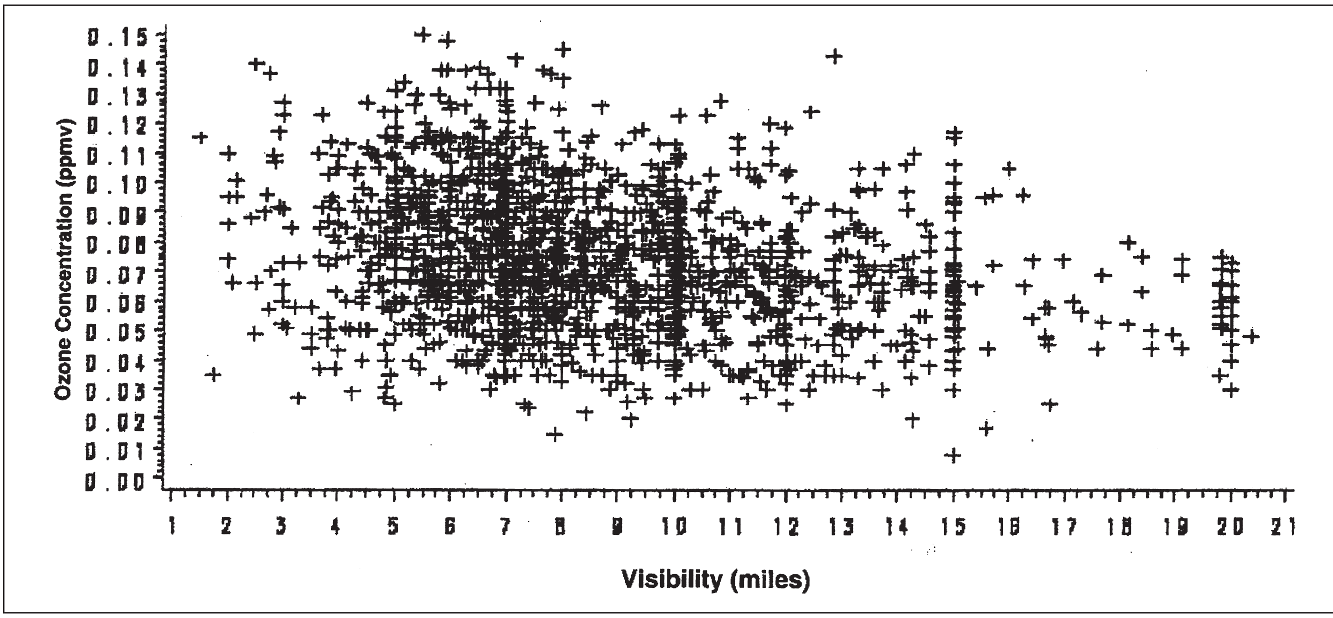

Figure 4. Scatter plot of hourly averaged observations for O_3 concentration vs. visibility in Nashville from 1980 to 1996.

Nashville Daily/Hourly Averaged Analysis

Regression analysis was performed utilizing daily average values grouped by month. The O_3 season for five arbitrarily selected above-normal O_3 years (based on yearly anomalies: 1980, 1983, 1988, 1990, and 1995) constituted the study period. The visibility and O_3 relationship became evident by this method. A statistically significant (α = 0.05) inverse relationship was displayed in 27% of these months, compared with no months when yearly average summaries were used (see Figure 6).

Regression analysis also was performed utilizing hourly values grouped by month. The visibility and O_3 relationship became more evident in this hourly value analysis. A statistically significant (α = 0.05) inverse relationship between O_3 and visibility was displayed in 60% of the years. However, the regression analysis remained noisy, which led to r^2 at or below 0.2. Similar results were obtained at the other areas comprising the Southeast United States Study Region (Charlotte, CLT; Raleigh, RDU; Greensboro, GSO; Atlanta, ATL). At these sites, r^2 between 0.03 and 0.43 were observed.

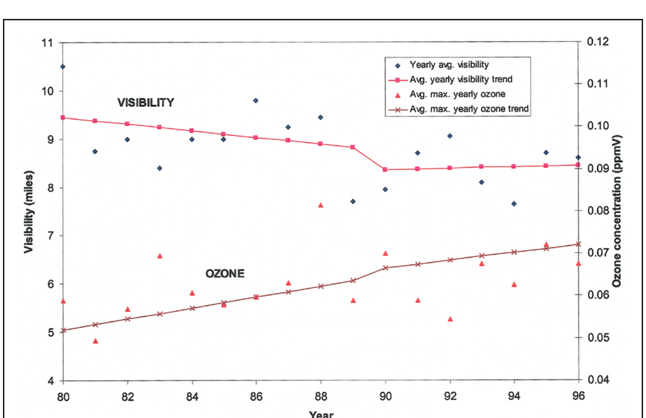

Figure 5. Yearly averaged O_3 and visibility trends for Nashville from 1980 to 1996.

Back Trajectory and Modeling Analyses

It was noted that the role of transport of high O_3 concentration and its precursors to various sites in the southeast United States may be more significant.[19,20] The gas-to-particle conversion processes, which produce secondary fine PM in the atmosphere, are generally slow relative to transport times; hence, visibility is considered a regional problem.[21]

Figure 7 shows the daily variations of average O_3 visibilities during August 1995 at Nashville. During this period, more than 80% of a negative relationship between O_3 concentration and visibility was observed. Back-trajectory analysis also was analyzed during this period. Back trajectories follow an air parcel backward in time to describe the path followed by the air parcel, ideally locating the source region of the air mass. Forty-eight-hour back-trajectory analysis (at 850 mb) was applied to the August 1995 daily analysis (see Figure 8). August 1995 displayed the highest correlation among the individual areas composing the southeast United States study region. Samplings of three backward trajectories are presented.

The analysis began on August 2, 1995. The air mass traveled through a moderately high source for VOCs, SO_2, and NO_x (as determined by EPA emission source maps—South Carolina and northern Georgia), which increased O_3. A consequence of this increased O_3 was the observed reduction in visibility during this same period (see Figures 7 and 9).

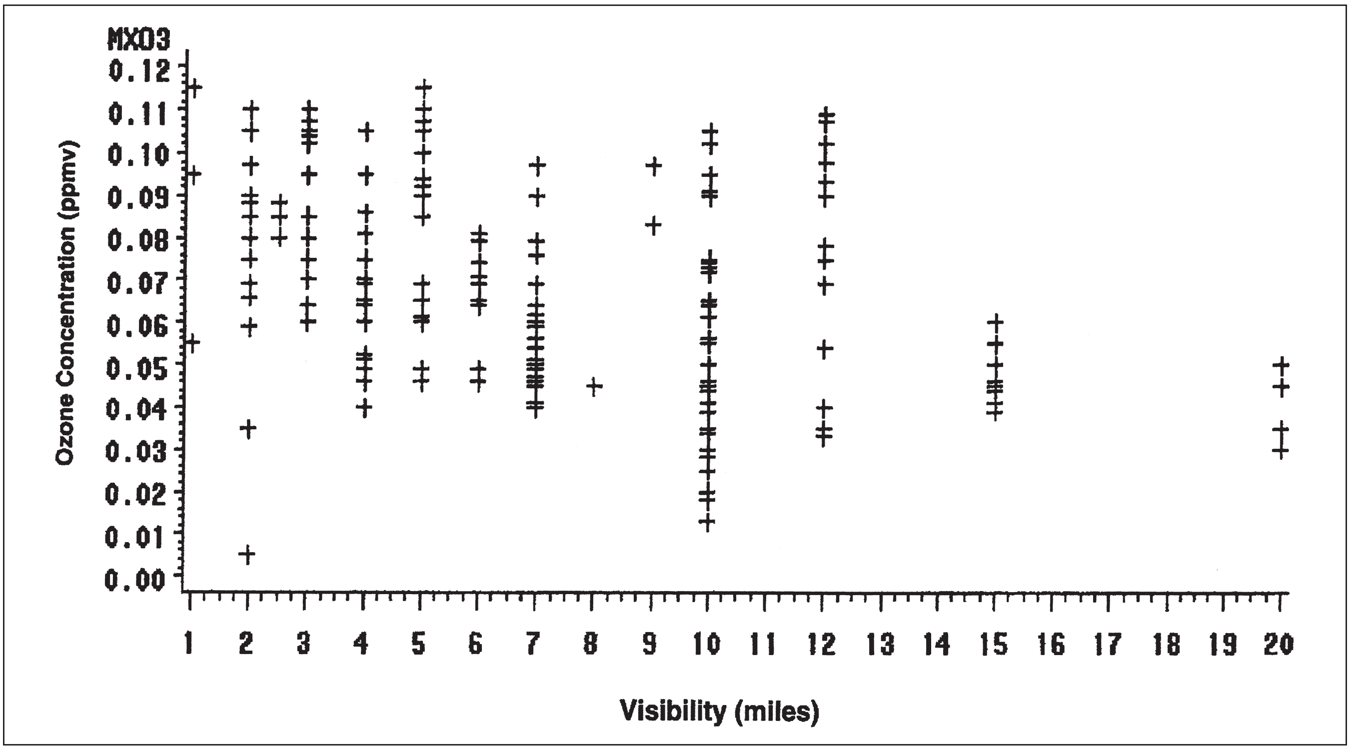

Figure 6. Scatter plot of hourly averaged observations for O_3 concentrations vs. visibility in Nashville during July 1983.

The model run for August 4, 1995 (see Figure 8) shows that the air parcel had covered a longer path length, implying quick travel time and a nonstagnating air mass. Additionally, the air mass had traveled over cleaner nonpolluted areas (Georgia and over the ocean). As a consequence, visibility increased and O_3 decreased

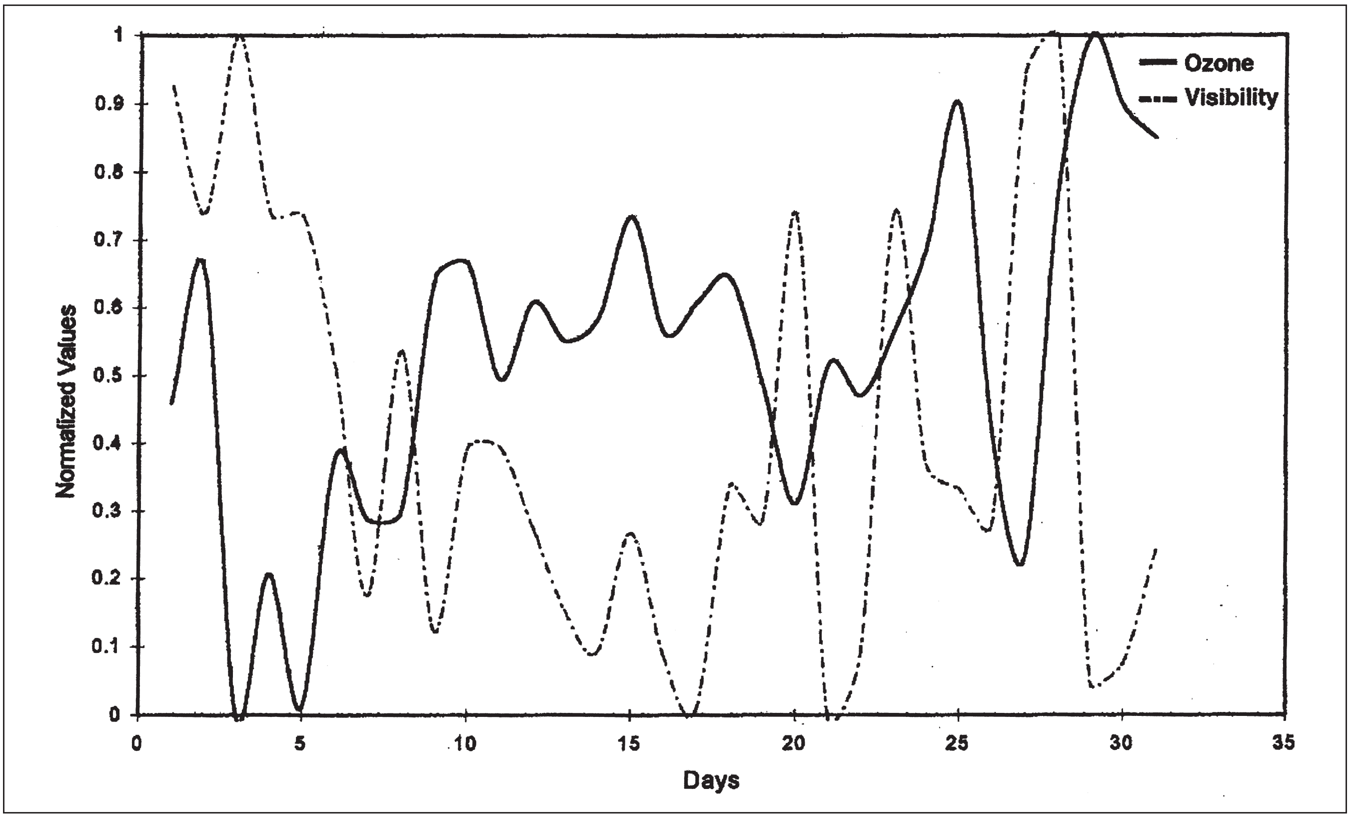

Figure 7. Nashville normalized daily averaged O_3 and visibility for August 1995. This month also was used for the back-trajectory analysis.

Figure 8. 48-hr back-trajectory analysis at 850 mb ending August 2, August 4, and August 30, 1995 (12 coordinated universal time).

(see Figures 7 and 9). These results also are supported by the simulation of the Multi-scale Air Quality Simulation Platform (MAQSIP), (see Figure 9a–9c). It must be noted that the August 2–4 analysis was affected by the development of hurricane Erin (July 31–August 6, 1995). Erin made landfall on August 2, 1995, near Vero Beach, FL, as a Category 1 hurricane.

In contrast to the long path length observed on August 4, 1995, the simulation run for August 30 (see Figure 8) was marked by a much shorter path length over a polluted area (industrial Midwest). The path is nondirect and meanders over polluted regions. The result is a stagnating air mass whose O_3 levels have increased and visibility decreased (see Figure 7).

CONCLUSIONS

The results obtained support the hypothesis that O_3 displays an inverse relationship with visibility. The overall regional O_3 trend appears to have increased during the 1980s (0.0005 ppmv/yr, $r^2 = 0.0497$) and leveled off during the 1990s (−0.00007 ppmv/yr, $r^2 = 0.0007$). Regional visibility trends during the 1980s decreased (−0.0222 mi/yr, $r^2 = 0.0426$) at a rate similar with the increasing O_3 trend. During the 1990s, the relationship weakened (0.0802 mi/yr, $r^2 = 0.3177$). Yearly trend analysis appears to support an inverse relationship; however, the data were not statistically significant utilizing the 5% level of significance. In Nashville, results were similar; however, O_3 levels continued to rise during the 1990s. This tended to

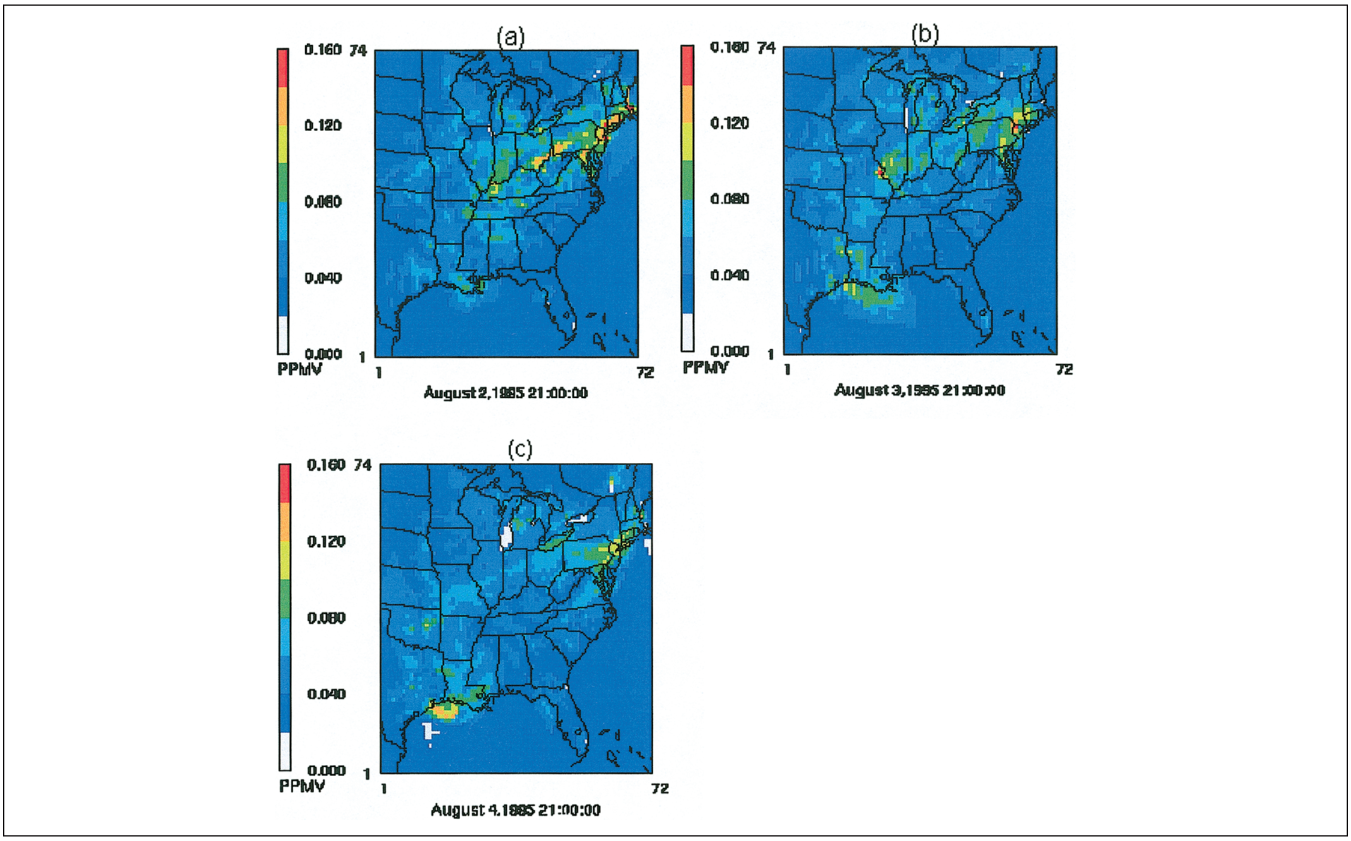

Figure 9. Near-surface O_3 concentrations simulated by MAQSIP during the August 1995 episode at 2100 coordinated universal time (a) August 2, (b) August 3, and (c) August 4.

suppress the evidence of an inverse O_3-visibility relationship during this period for Nashville.

The statistical significance of the analysis (at the 0.05 level) improved (became statistically significant at $\alpha = 0.05$) when temporal resolution was measured in days and hours and spatial resolution was reduced to specific areas (nonregional). A statistically significant inverse relationship was observed 27% of the time (15 months; ~30 observations/month) when linear regression was performed on Nashville data utilizing daily averaged observations grouped by month. Nashville r^2 values ranged from 0.02 to 0.24 for O_3 versus visibility utilizing these daily averaged values. Statistical significance was observed 60% of the time (15 months; ~200 observations/month). For these locations (RDU, CTL, GSO, and ATL), r^2 values ranged from 0.03 to 0.43 collectively. Nashville r^2 values were less than 0.2.

These findings are also similar to the results of other research. Results of a 2-year study in the Netherlands showed a relationship between visibility, PM, and O_3.[22] Modeling runs also suggest the lowest visibility correlates best with peaks in O_3 and SO_4^{2-} (fine PM).[23]

Yearly regional anomaly comparison showed a good agreement between O_3 and temperature and an inverse relationship between O_3 and relative humidity. However, a consistent relationship was not observed between visibility and O_3. Site-specific yearly anomaly analysis showed an even less distinctive pattern of correlation. Relative humidity did, however, appear to impact visibility correlations at Nashville more than in the region as a whole. Site-specific yearly anomaly analysis was performed only for the Nashville Metropolitan Statistical Area (MSA).

Back-trajectory and modeling analyses showed that slow-moving meandering air masses produced higher levels of O_3 and lower visibilities. In fact, the study month (August 1995) had persistent high-pressure systems throughout the region, which elevated O_3 and reduced visibility at nearly all of the locations. Air mass source regions also influenced this relationship, with air masses passing over more polluted areas having an impact on both O_3 levels and visibility.

ACKNOWLEDGMENTS

The North Carolina Department of Environmental Health provided partial funding for this research and Natural Resources (Contract EA 01001), and A. Hanna would also like to acknowledge the National Science Foundation for support under grant INT–9904792. The authors also gratefully acknowledge the support provided by MCNC-Environment Programs in performing and analyzing model results. Computer support was provided by the North Carolina Supercomputer Center. Thanks to Ms. M. DeFeo, Ms. S. Phillips, and Mrs. P. Aneja for the word processing of the manuscript.

REFERENCES

1. Southern Appalachian Man and the Biosphere. *The South Appalachian Assessment Atmospheric Technical Report*; Report 3 of 5; U.S. Department of Agriculture, Forest Service, Southern Region: Atlanta, GA, 1996.
2. Middleton, P.; Stewart, T.R.; Dennis, R.L. Modeling Human Judgments of Urban Air Quality; *Atmos. Environ.* **1984**, *17*, 1015-1021.
3. U.S. Environmental Protection Agency. http://134.67.104.12/naaqspro/o3hlth.htm (accessed 1997).
4. Hagen-Smit, A.J. Chemistry and Physiology of Los Angeles Smog; *Ind. Eng. Chem.* **1952**, *44*, 1342-1346.
5. Meng, Z.; Dabdub, D.; Seinfeld, H. Chemical Coupling between Atmospheric Ozone and Particulate Matter; *Science* **1997**, *277*, 116-119.
6. Friedlander, S.K. *Smoke, Dust and Haze;* Wiley: New York, 1977.
7. Trijonis, J. Existing and Natural Background Levels of Visibility and Fine Particles in the Rural East; *Atmos. Environ.* **1982**, *16*, 2431-2445.
8. Husar, R.B.; Wilson, W.E. Haze and Sulfur Emission Trends in the Eastern United States; *Environ. Sci. Technol.* **1993**, *27*, 12-16.
9. Parkhurst, W.J.; Tanner, R.L.; Weatherford, F.P.; Balente, R.J.; Meaghet, J.F. Historic $PM_{2.5}/PM_{10}$ Concentrations in the Southeastern United States–Potential Implications of the Revised Particulate Matter Standard; *J. Air & Waste Manage. Assoc.* **1999**, *49*, 1060-1067.
10. Finlayson-Pitts, B.; Pitts, J.N. *Atmospheric Chemistry: Fundamental and Experimental Techniques*; Wiley: 1986.
11. Granier, C.; Brasseur, G.; Erickson, D. In *Atmospheric Chemistry and Global Change*; Brasseur, G., Orlando, J.J., Tyndall, G.S., Ed.; Topics in Environmental Chemistry; Oxford University Press: New York, 1999; pp 530-536.
12. Middleton, P. DAQM-Simulated Spatial and Temporal Differences among Visibility, PM, and Other Air Quality Concerns under Realistic Emission Change Scenarios; *J. Air & Waste Manage. Assoc.* **1997**, *47*, 302-316.
13. O'Conner, J. A Climatology of Regional Ozone: Meteorological Effects on Ozone Exceedences in the Southeast United States. Master's Thesis. Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC, 1996.
14. *Federal Meteorological Handbook No. 1, Surface Weather Observations and Reports*; U.S. DOC/NOAA, Washington, DC, 1995.
15. National Research Council. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*; National Academy Press: Washington, DC, 1991.
16. Logan, J.A.; Prather, M.J.; Wofsy, S.C.; NcElroy, M.B. Tropospheric Chemistry: A Global Perspective; *J. Geophys. Res.* **1981**, *86*, 7210-7254.
17. Chameides, W.L.; Lindsay, R.W.; Richardson, J.L.; Kiang, C.S. The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study; *Science* **1988**, *241*, 1473-1475.
18. Aneja, V.P.; Arya, S.P.; Li, Y.; Murray, G.C.; Manuszak, T.L. Climatology of Diurnal Trends and Vertical Distribution of Ozone in the Atmosphere Boundary Layer in Urban North Carolina; *J. Air & Waste Manage. Assoc.* **2000**, *50*, 54-64.
19. Lindsay, R.W.; Richardson, J.L.; Chameides, W.L. Ozone Trends in Atlanta, Georgia: Have Emission Controls Been Effective; *J. Air Pollut. Control Assoc.* **1989**, *39*, 40-43.
20. Aneja, V.P.; Li, Z.; Das, M. Ozone Case Studies at High Elevation in the Eastern United States; *Chemosphere* **1994**, *29*, 1711-1733.
21. Gray, H.A.; Kleinhesselink, D. *Evaluation of Existing Information on the Effects of Air Pollution on Visibility in the Southern Appalachians*; Final Report; Systems Applications International: San Rafael, CA, October 1996.
22. Diederen, H.S.M.A.; Guicherit, R.; Hollander, J.C.T. Visibility Reductions by Air Pollution in the Netherlands; *Atmos. Environ.* **1985**, *19*, 377-383.
23. King, W.J.; Vukovish, F.M. Some Dynamic Aspects of Extended Pollution Episodes; *Atmos. Environ.* **1982**, *16*, 1171-1181.

About the Authors

Viney P. Aneja is a professor, Jeffrey S. Brittig is a graduate research assistant, and Deug-Soo Kim is a visiting research associate professor in the Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208. Dr. Kim's permanent affiliation is as an associate professor in the Department of Environmental Engineering, Kunsan National University, Kunsan, Chonbuk 573–701, Korea. Adel Hanna is with Carolina Environmental Program, University of North Carolina, Chapel Hill, NC 27599. Address correspondence to Dr. Viney P. Aneja, fax: (919) 515-7802; e-mail: viney_aneja@ncsu.edu.