The Impact of Background Ozone on Compliance with Revised National Ambient Air Quality Standards

David J. Williams
Oklahoma State University, Stillwater, OK

William T. Potter
University of Tulsa, Tulsa, OK

William W. Clarkson
Oklahoma State University, Tulsa, OK

Dee A. Sanders and John E. Stevens
Oklahoma State University, Stillwater, OK

ABSTRACT
The National Ambient Air Quality Standard (NAAQS) for ground-level ozone, previously set as an 8-hr average of 0.08 parts per million (ppm), has been revised by the U.S. Environmental Protection Agency (EPA). Historically, background concentrations originating from non-local sources were not considered to be a major constituent of ground-level ozone. However, previous research has shown that background ozone concentrations often exceed the new 8-hr NAAQS of 0.075 ppm, and that high background concentrations are particularly troublesome in the mid-latitudes. This study measured ozone at ground level and at 210 m above ground level in Tulsa, OK (36°N, 96°W), from June 1 to November 30, 2005. Background ozone concentrations as high as 0.05 ppm were recorded, and substantial variability was observed in conjunction with the polar jet stream and the seasonal influence of large-scale subtropical high pressure at the study location. Additionally, the highest observed background concentrations coincided with maximum photochemical generation at ground level. On the basis of the magnitude and variability of background ozone, a more stringent 8-hr ozone standard will be difficult for local or regional regulatory agencies to meet. A clear understanding of the impacts of background ozone will be required to make and meet new State Implementation Plans (SIPs).

INTRODUCTION
Ozone (O₃), a criteria air pollutant as defined by the Clean Air Act (CAA), is subject to regulation in accordance with the National Ambient Air Quality Standards (NAAQS). The U.S. Environmental Protection Agency (EPA) has revised the O₃ NAAQS, setting the primary (health) standard at 0.075 parts per million (ppm). This reduction of the 8-hr O₃ NAAQS approaches the current 8-hr standards of the European Union (0.061 ppm), Canada (0.065 ppm), and California (0.07 ppm). The EPA Clean Air Scientific Advisory Committee (CASAC), an independent oversight board whose authority stems from CAA Section 109(b), has endorsed this revision of the O₃ NAAQS, solely on the basis of the health-related effects of O₃. Meeting the proposed 8-hr O₃ standard will have significant impact on regulatory agencies, metropolitan areas, industries, and the public sector. A clear understanding of the non-local natural and anthropogenic sources that constitute background O₃ will be required to make and meet new State Implementation Plans (SIPs) under Title 40 of the Code of Federal Regulations (40 CFR), Part 51. Dealing with background O₃ will likely require a coordinated national effort for O₃ control strategies.

HISTORY OF THE O₃ STANDARD
The O₃ NAAQS, established on April 30, 1971 in Section 109 of the CAA, set a 1-hr standard of 0.08 ppm. Following a review of the original standard, the 1-hr standard was subsequently increased to 0.12 ppm on February 8, 1979 in response to what was then known about O₃ exposure and public health. Penalties for nonattainment listed in 40 CFR Part 51.900 include the implementation of reasonably available control technologies, vehicle inspection and maintenance programs, vapor recovery systems at fueling stations, transportation control measures,
and increased air quality monitoring. In the 1997 review of the \( O_3 \) NAAQS, a new 8-hr standard of 0.08 ppm was promulgated and has supplanted the 1-hr standard in most locations.

According to 40 CFR Part 50.9(b), “…the 1-hr NAAQS set forth in paragraph (a) of this section will no longer apply to an area one year after the effective date of the designation of that area for the 8-hr ozone NAAQS pursuant to section 107 of the Clean Air Act…” On the basis of this provision, the 1-hr \( O_3 \) NAAQS became obsolete on June 15, 2005. If a metropolitan statistical area is designated as not meeting the 8-hr standard, then measures must be taken to achieve compliance. Following legal challenges, the EPA reviewed the 8-hr \( O_3 \) NAAQS (a 5-yr CAA requirement) and a revised standard was published on March 12, 2008.

**Prior Research on Background \( O_3 \)**

The potential for \( O_3 \) production in the lower atmosphere is governed not only by local sources, but also by sources of non-local origin that include natural and anthropogenic \( O_3 \) as well as precursor compounds that are required for photochemical reaction. Research has shown that this non-local or “background” \( O_3 \) concentration is transported in large-scale air masses and may be estimated by direct measurements of \( O_3 \) within the middle part of the troposphere. \( O_3 \) molecules at these elevations can exist for longer periods than at ground level, because they are neither subjected to appreciable dry deposition nor to titration from ground-level nitrogen oxide (NO), and unlike ground-level \( O_3 \), low-level temperature inversions do not restrict background \( O_3 \) from its source.

\( O_3 \) concentrations in the lower atmosphere resulting solely from natural sources have been estimated in the range of 0.01–0.04 ppm. There values are consistent with early measurements of background \( O_3 \), which were found to range between 0.01 and 0.05 ppm (with most values between 0.01 and 0.03 ppm). However, little attention was paid to the role that these concentrations play in the daily evolution of ground-level \( O_3 \). Subsequent observations of background \( O_3 \) were higher, with reported maximum concentrations of 0.08 ppm, representative of \( O_3 \) from non-local natural and anthropogenic sources.

Contemporary reports of background concentrations vary (Table 1), but all values given in recent literature are relatively high downwind of industrialized areas and in regions with high natural volatile organic compound and photochemical production potential. In 1995, the North American Research Strategy for Tropospheric Ozone (NARSTO) campaign examined the presence of an \( O_3 \) reservoir along the Atlantic Coast of the United States, where background concentrations varied between 0.08 and 0.10 ppm. Background concentrations in the eastern Atlantic were similar to those in southwestern Europe, with measured values between 0.05 and 0.07 ppm.

A study in Taiwan measured background \( O_3 \) concentrations between 0.078 and 0.086 ppm in a layer between 600 and 900 m above ground level. In Spain, the nocturnal (background) \( O_3 \) concentration varied between 0.06 and 0.08 ppm. Likewise, \( O_3 \) is not limited to populated, industrialized areas. Concentrations as high as 0.04 ppm have been measured north of the Arctic Circle in Greenland during the winter months.

Previous research in Oklahoma found that higher \( O_3 \) concentrations were prevalent immediately above the low-level temperature inversion within the nocturnal boundary layer, where background concentrations as high as 0.070 ppm were commonly measured. High \( O_3 \) concentrations within the nocturnal boundary layer are an indicator of regional transport processes, and are thus not of local origin. \( O_3 \) production from local, short-term photochemistry combines with the background concentration, contributing to the total \( O_3 \) in a particular location at any given time.

In terms of ground-level concentrations, background \( O_3 \) and its precursor compounds are at least as important as local photochemical production. \( O_3 \) concentrations recorded with aircraft instrumentation within the upper troposphere were as high as 0.125 ppm. Contributions from transported \( O_3 \) to the total ground-level concentration in North Carolina have been estimated as high as 50%. Similarly, 40% of total ground-level \( O_3 \) was attributed to transported \( O_3 \) in Taiwan. A significant component of ground-level \( O_3 \) in New England is thought to be of remote origin as well, with baseline concentrations

<table>
<thead>
<tr>
<th>Reference</th>
<th>Location</th>
<th>Elevation (m)</th>
<th>Interval</th>
<th>Type</th>
<th>Concentration Range (ppm)</th>
<th>Upper Bound (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plaza et al.16</td>
<td>Spain</td>
<td>&gt;300</td>
<td>July 12, 1994 to July 19, 1994</td>
<td>Aircraft</td>
<td>0.06–0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Ryan et al.36</td>
<td>Mid-Atlantic (United States)</td>
<td>600–1200</td>
<td>July 12, 1995 to July 15, 1995</td>
<td>Aircraft</td>
<td>0.06–0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Zhang et al.7</td>
<td>New York (United States)</td>
<td>500–1000</td>
<td>July 12, 1995 to July 16, 1995</td>
<td>Aircraft</td>
<td>0.08–0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Baumann et al.27</td>
<td>Tennessee (United States)</td>
<td>&lt;1490</td>
<td>July 30, 1994 to July 2, 1994</td>
<td>Aircraft</td>
<td>0.06–0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Gangoiti et al.14</td>
<td>Italy</td>
<td>&lt;3000</td>
<td>July 16, 1991 to July 19, 1991</td>
<td>Aircraft</td>
<td>0.05–0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Kastner-Klein et al.2</td>
<td>Oklahoma (United States)</td>
<td>460</td>
<td>August 31, 1998 to September 6, 1998</td>
<td>Fixed</td>
<td>0.01–0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Dayan and Levy29</td>
<td>Israel</td>
<td>N/A</td>
<td>January 1997 to December 1999</td>
<td>Fixed</td>
<td>0.01&lt;0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Heidam et al.17</td>
<td>Greenland</td>
<td>GLb</td>
<td>January 1, 1999 to September 27, 2001</td>
<td>Fixed</td>
<td>0.02–0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Lin et al.15</td>
<td>Taiwan</td>
<td>600–900</td>
<td>December 14, 2002 to December 15, 2002</td>
<td>Ozone sonde</td>
<td>0.08–0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Williams et al.42</td>
<td>Oklahoma (United States)</td>
<td>210</td>
<td>June 1, 2005 to November 30, 2005</td>
<td>Fixed</td>
<td>0.01&lt;0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Notes: Background \( O_3 \) concentrations measured as the residual concentration above the nocturnal low-level temperature inversion. Background concentrations of \( O_3 \) in the Arctic are measured at ground level (GL). Averaging times for mobile measurements (aircraft, ozonesonde) were on the order of seconds; fixed measurement averaging times ranged from 30 min (Dayan and Levy29) to 1 hr (Kastner-Klein et al., Williams et al.42). No averaging time was listed for Heidam et al.17
Background O3 and Meteorology

The origins of background O3 are not fully understood, but certain meteorological regimes are likely contributors. In particular, subtropical high-pressure systems are known to coincide with episodes of ground-level O3 pollution.14,16,18,25–34 High-pressure systems are synonymous with large-scale subsidence through the troposphere, coinciding with stagnant conditions at Earth’s surface. High concentrations of O3 have been associated with high-pressure systems and attendant subsidence, particularly when the anti-cyclical circulation surrounding the center of high pressure is weak, leading to calm winds, sunny skies, and warm temperatures at ground level.35

Many international studies have noted the connection between subtropical high-pressure systems and episodes of high ground-level O3, ranging from the Azores High in western Europe to the Asian High in China.14–16,18,25,26,28,30,32 The relationship between high-pressure systems and high O3 concentrations has also been observed in the United States. A study in Nashville, TN, found that high pressure aloft and subsequent stagnation of the boundary layer increases the likelihood of high levels of ground-level O3.27 Similar high-pressure regimes contribute to O3 increase on the Pacific Coast of the United States, where the Pacific High tends to dominate.31 The presence of the Pacific High, a broad, anticyclonic circulation, promotes stagnation within the boundary layer in the Los Angeles metropolitan area.31 The Pacific High is marked by strong subsidence through the troposphere.32 In the south-central United States, a possible contribution of O3 in Louisiana results from horizontal advection around the Bermuda High from sources in southeastern Texas.34 As the Bermuda High shifts eastward, lower concentrations of O3 appear to enter the region from the Gulf of Mexico.34 Mid-Atlantic air pollution episodes also intensify from synoptic anticyclonic circulations as O3-rich air propagates into the Baltimore-Washington, DC, corridor under the influence of high pressure.7,36

Stratospheric-tropospheric exchange (STE) is a mechanism that potentially contributes significant O3 concentrations to the troposphere.11,25,37 When a strong, detached low-pressure system is present in the middle atmosphere, the height of the troposphere, or tropopause,descends behind the center of the cyclonic circulation.38 In this scenario, exchange between the stratosphere and troposphere occurs as the tropopause folds underneath the upper-level cyclone or an attendant upper-level trough.39,40 These meteorological features are commonly in close proximity to the upper-level jet stream.40 Tracer studies of beryllium-7 have shown that stratospheric O3 transported through STE is a source of O3 in the troposphere.41 High concentrations of O3 in Korea have been recorded in the presence of a cutoff low—a cyclical circulation detached from the mean mid-level flow.39 A similar synoptic pattern, marked by a cutoff low-pressure system, resulted in increased O3 concentrations in the Pyrenees Mountains of Spain.38 Observations of high O3 concentrations on the western sides of upper-level cyclones in the North Atlantic indicate that stratospheric O3 is entering the troposphere through tropopause folds in these regions as a function of STE.18

Background O3 is therefore dynamically driven by the polar jet stream, and with the seasonal northward shift of the polar jet during the summer, O3 concentrations in the mid-latitudes increase near ground level as a result of the influence of subtropical high pressure.42 These episodes are often several weeks in duration, because subtropical high-pressure systems tend to be persistent. When this synoptic meteorological regime ensues, background O3 concentrations increase as a result of large-scale subsidence, whereas local photochemical O3 production increases in response to sunny, stagnant conditions that typically accompany high pressure.

Methodology

O3 analyzed in this study was measured as the nocturnal minimum concentration at an elevation of 210 m above ground level in a similar manner to several of the previous studies cited in this paper. Acquisition of the data was coordinated with the Oklahoma Department of Environmental Quality, and all measurement techniques adhered to the EPA Equivalent Method EQOA-0880-047 for the measurement of ambient concentrations of O3 as described in 40 CFR Part 53.43

New Findings

With a research interval of 6 months, a high degree of variability was observed in the background O3 trend, which was estimated as the minimum nocturnal concentrations at 210 m above ground level (Figure 1). Under the influence of strong subsidence associated with subtropical high-pressure systems, background values in the range of

Figure 1. Hourly boundary-layer O3 concentrations measured at ground level and at 210 m above ground level in Tulsa, OK, during the 2005 O3 season. Minimum nocturnal concentrations at 210 m represent background O3 in the troposphere.
0.02–0.05 ppm were commonly observed during the summer months in Tulsa, OK, a mid-sized metropolitan area situated at 36 °N, 96 °W. Low background O₃ concentrations measured in the range of 0.01–0.02 ppm coincided with the passages of upper-level cyclones and troughs. Overall, background O₃ concentrations measured during the study exhibited relative increases and decreases observed in conjunction with the passages of high- and low-pressure systems, respectively. An illustrative example of this relationship occurred between July 18 and 27, 2005 when the passage of a high-pressure system was preceded and followed by the passages of low-pressure systems (indicated by fluctuations in the 300-hPa geopotential heights at 46 °N, representative of the height of the polar jet stream), subsequently affecting the 210-m O₃ concentration. Proximity to the polar jet stream was particularly important, because long-duration episodes of high background concentrations (and ground-level pollution) corresponded with the seasonal summer retreat of the polar jet in the mid-latitudes as large-scale subtropical high-pressure systems advanced northward. The end of summer brought the gradual return of the polar jet to 36 °N, marking the end of subtropical high-pressure systems advanced northward.

A strong connection exists between background O₃ (measured as a component of 210-m O₃) and ground-level O₃, which vigorously mix following the daily development of the atmospheric boundary layer. Correlation between the two levels was highest during a 9-hr daytime interval beginning at 8:00 a.m. central standard time (CST) and ending at 5:00 p.m. CST. Although appreciable solar radiation (>100 W · m⁻²) exceeds 13 hr/day during the summer months at 36 °N, the smaller daily interval of 9 hr is representative of late fall, including the data measured in November. O₃ concentrations measured at 210 m were paired with ground-level O₃ from the previous hour, allowing for vertical mixing between the two elevations. A linear response was observed, and the coefficient of determination (R²) equaled 0.8781 (Figure 3). The well-mixed O₃ reservoir encompassing the two heights generally developed within 2 hr of sunrise when the structure of the atmospheric boundary layer transitioned from a decoupled low-level stable nocturnal boundary layer and overlying residual layer to a coupled, convectively driven mixed layer in the lower atmosphere. Therefore, background O₃ and precursor compounds mix to the surface during the development of the atmospheric boundary layer, contributing to the daily O₃ maximum at ground level. Background concentrations as high as 0.05 ppm were observed in conjunction with maximized local photochemical generation, which combined for total concentrations in excess of 0.1 ppm.

**CONCLUSIONS**

This study found that background O₃ in the atmospheric boundary layer, measured as the nocturnal minimum concentrations at 210 m, is a variable quantity that is...
highly dependent upon large-scale meteorological processes. The background O₃ concentration was clearly observed in the 210-m data, because the nocturnal minimum commonly ranged between 0.02 and 0.05 ppm during the study. Conversely, O₃ concentrations at ground level were strongly diurnal, approaching 0 ppm during the overnight hours. Therefore, ground-level O₃ is not solely a product of local photochemistry, but instead is a combination of local sources and large-scale vertical transport that mixes boundary-layer O₃ with ground-level O₃ and related precursor compounds.

With the approach of subtropical high-pressure systems, not only did large-scale subsidence lead to an increase in background O₃ concentrations, but an enhancement of local photochemistry occurred as well, because low wind speeds, low relative humidity, and increased solar radiation and air temperature—all characteristics of high-pressure regimes—contributed to high O₃ concentrations at ground level. Therefore, episodes of large-scale high pressure provide an optimal scenario for high boundary-layer O₃ concentrations, particularly during the summer months when semipermanent subtropical highs migrate into the mid-latitudes. During these conditions, background O₃ accumulates as a result of large-scale subsidence, whereas photochemical production maximizes at ground level. This combination of high background and locally produced O₃ results in air pollution episodes of increasing severity. The effects that subtropical high-pressure systems and related weather patterns have on boundary-layer O₃ concentrations decrease with the seasonal return of the polar jet stream, although weaker high-pressure systems do result in increased background concentrations. These systems are not persistent, however, and the likelihood of a long-duration O₃ pollution episode is low outside of the summer months.

On the basis of a comparison of background O₃ to the total ground-level O₃ concentration measured in Tulsa, local production only appears to account for as much as 50% of the total, with the highest concentrations observed during meteorological conditions that accompany subtropical high-pressure systems. Although toxicological studies play an important role in the EPA review of the O₃ NAAQS, consideration should be given to the behavior of the background O₃ concentration, which contributes significantly to ground-level O₃ readings. Research evidence suggests that the dynamic background O₃ concentration in the mid-latitude atmospheric boundary layer approaches and occasionally exceeds 0.05 ppm.

The implementation of a new O₃ NAAQS will undoubtedly place an increased attainment burden on many localities in the United States, because a narrow margin will exist between the proposed NAAQS revision and background O₃ concentrations that have been observed in multiple air quality studies. Although an increasingly stringent standard may be more attainable at higher latitudes (similar to those set in Canada and the European Union), compliance will be a challenge in the mid-latitudes. As a provision of the CAA, state regulatory agencies must develop a SIP for areas that fail to comply with the NAAQS. Proposed compliance strategies are a component of the SIP, and in light of the substantial role that background O₃ plays in ground-level O₃ concentrations and subsequently NAAQS compliance, these plans must account for the relationship between background and ground-level O₃.

Strategies designed for the reduction of ambient ground-level O₃ concentrations and subsequent improvement of the nation’s air quality must diverge from the conventional view of O₃ as a local contaminant. Instead, ground-level concentrations are strongly influenced by background O₃, which is governed by large-scale meteorological processes. Dealing with background O₃ will likely require a coordinated national effort for O₃ control strategies that build upon the framework established by collaborative multi-agency research efforts such as NARSTO. On the basis of the new O₃ 8-hr NAAQS, we suggest that prolonged episodes of high background concentrations may result in an unattainable O₃ standard for many locations in the mid-latitudes.

ACKNOWLEDGMENTS

This research was funded in part by EPA Greater Research Opportunities (GRO) Fellowship Program (MA-91658301-0), Sigma Xi Grants in Aid of Research, the Oklahoma Department of Environmental Quality, and the City of Tulsa, OK.

REFERENCES

1. Plan for Review of the National Ambient Air Quality Standards for Ozone; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 2005.
5. Review of the National Ambient Air Quality Standards for Ozone; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 2007.


38. Tulet, P.; Suhre, K.; Mari, C.; Solmon, F.; Rosset, R. Mixing of Boundary Layer and Upper Tropospheric Ozone during a Deep Convective Event over Western Europe; Atmos. Environ. 2002, 36, 4491-4501.


42. Williams, D.J. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK, 2007.


About the Authors

David J. Williams is an adjunct professor in the Department of Civil and Environmental Engineering at Oklahoma State University. Dee A. Sanders and William W. Clarkson are associate professors in the Department of Civil and Environmental Engineering at Oklahoma State University. John E. Stevens is an assistant professor in the Division of Engineering Technology at Oklahoma State University. William T. Potter is a professor in the Department of Chemistry and Biochemistry at the University of Tulsa. Please address correspondence to: Dr. David J. Williams, Department of Civil and Environmental Engineering, Oklahoma State University, 700 North Greenwood Avenue, Tulsa, OK 74106-0700; phone: +1-918-594-8304; fax: +1-918-594-8558; e-mail: david.williams@okstate.edu.