Intraseasonal variability of surface ozone in Santiago, Chile: Modulation by phase of the Madden–Julian Oscillation (MJO)

Bradford S. Barrett\textsuperscript{a,}*, Sean J. Fitzmaurice\textsuperscript{b}, Sarah R. Pritchard\textsuperscript{a}

\textsuperscript{a}Oceanography Department, U.S. Naval Academy, 572C Holloway Rd., Annapolis, MD 21401, USA
\textsuperscript{b}Naval Nuclear Power Training Command, Charleston, SC, USA

HIGHLIGHTS

\begin{itemize}
  \item Surface ozone concentration in Santiago, Chile varies intraseasonally by phase of the Madden–Julian Oscillation.
  \item Phase of the Madden–Julian Oscillation also affects the diurnal cycle of ozone concentration in Santiago.
  \item Days with low (high) ozone corresponded to days with anomalously high (low) cloud cover.
\end{itemize}

ABSTRACT

In Santiago, Chile, summertime surface ozone (O\textsubscript{3}) concentrations regularly exceed local and international health thresholds due to high antecedent pollutants, frequent clear skies, and warm surface air temperatures. However, few (if any) studies exist that have examined the intraseasonal variability of surface O\textsubscript{3} or its modulation by phase of the Madden–Julian Oscillation (MJO). Therefore, the main objectives of this study were to investigate the intraseasonal variability of surface O\textsubscript{3} and the meteorological parameters known to affect O\textsubscript{3} concentrations during summer months in Santiago, and connect any observed variability to phase of the MJO. Ozone concentrations at seven stations in the Chilean National Air Quality Information System (SINCA), along with upper-air, surface, and reanalysis data, were used to create composites for each phase of the MJO. Results confirm that for the Santiago metropolitan region, both maximum daily O\textsubscript{3} concentrations, as well as the diurnal cycle of O\textsubscript{3}, depend on MJO Phase. Ozone concentrations were highest during Phases 5 and 6 and lowest during Phases 1 and 2. Cloud cover anomalies best agreed with this pattern of O\textsubscript{3} variability, with low (high) cloud cover anomalies occurring during days with high (low) ozone. Surface temperature and strength and height of the lower-troposphere temperature inversion had similar, but less pronounced, connections to O\textsubscript{3}, with slightly warmer surface temperatures and stronger inversions closer to the ground occurring on days with higher O\textsubscript{3}. Wind velocity was found to vary little between days with low and high ozone.

1. Introduction

Ozone (O\textsubscript{3}) is one of the most important trace gases in the troposphere. As a secondary pollutant, its concentrations are controlled by complex processes involving anthropogenic emissions, chemical reactions between primary pollutants and ultraviolet solar radiation, and meteorology. It strongly affects human health, vegetation, and ecosystems in industrial, suburban, and rural areas worldwide and is expected to increase significantly during the 21st century. In Santiago, Chile, maximum hourly O\textsubscript{3} concentrations regularly reach between 100 and 150 parts per billion by volume (ppbv) in summer, occasionally peaking above 320 ppbv in the eastern (downwind) part of the city (Gramsch et al., 2006), well in excess of Chilean (0.075 ppmv hourly maximum) and U.S. (0.08 ppmv 8-h concentration) health thresholds. Ozone exposure at these levels produces harmful structural changes in human cells, specifically lesions in the centriacinar area of the lungs at the ends of the terminal bronchioles (Lippmann, 1989; Burnett et al., 1997). These effects cause respiratory problems, especially in those with chronic lung diseases, and can seriously damage the lining of the lung when inhaled over a long-period of time (Sanhueza et al., 2003). Even short-term (daily and weekly) exposure to ambient tropospheric O\textsubscript{3} has been associated with adverse effects on public health and increased mortality (Bell et al., 2004). For all these reasons, studies that determine the behavior of O\textsubscript{3} across a range of temporal and spatial scales are important.
However, intraseasonal variability of ground-level $O_3$ has yet to be comprehensively examined. Therefore, the main objectives of this study were to (1) investigate the intraseasonal variability of surface $O_3$ and related meteorological parameters during summer months in Santiago, Chile, and (2) connect any observed variability to phase of the leading mode of atmospheric intraseasonal variability, the Madden–Julian Oscillation (MJO; Madden and Julian, 1971).

The MJO manifests itself as a large-scale convective anomaly over the maritime continent. Its most basic feature consists of an eastward moving region of deep convective clouds and heavy precipitation bounded on both the west and east by regions of suppressed convection and minimal precipitation. Zonal circulations connect the two regions, with lower-tropospheric (near 850-hPa; anomalous westerly (easterly) winds to the west (east) of the deep convection; in the upper troposphere (near 200-hPa), the circulation anomalies reverse (Madden and Julian, 1972). The convective anomalies have been observed to remain between the Indian Ocean and 180°, while the circulation anomalies have been observed to circumnavigate the tropics.

The oscillation has significant interaction with the extratropics, including teleconnections to the Western Hemisphere. Modeling studies of Berbery et al. (1992) and Mechoso et al. (1991), as well as the hemispherical findings of Hoskins and Karoly (1981) and Bladé and Hartmann (1995), confirmed that the MJO modulates Rossby wave activity. Sardeshmukh and Hoskins (1988) found a pathway to the extratropics in both hemispheres, noting that a divergence field in easterly flow asymmetric about the Equator (a consequence of deep convection) led to an extremely effective Rossby wave source in the subtropical westerlies. Barrett et al. 2012 used this pathway to explain modulation of winter precipitation in Chile by phase of the MJO. A similar technique was used for this study to explain the link between intraseasonal ground-level $O_3$ variability in Santiago and the MJO. Detailed reviews of the MJO are presented in Madden and Julian (1994), Lau and Waliser (2005), and Zhang (2005).

During austral summer, central Chile frequently experiences clear skies and high temperatures due to the presence of the subtropical anticyclone centered in the southeast Pacific Ocean (Schmitz, 2005; Rutllant and Garreaud 2004; Garreaud and Muñoz, 2005). Additionally, because of a persistent low-level inversion and its orographic location at the rim of the highest peaks of the Andes Mountains, Santiago is a poorly ventilated location. Furthermore, low morning mixing heights, a result of the presence of a coastal trough immediately west of central Chile, often result in above normal afternoon surface temperatures, reaching between 30° and 35 °C in Santiago (Rappenglück et al., 2000). Surface $O_3$ production under these conditions is favored, as the photochemical oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) occurs in the presence of high concentrations of nitrogen oxides (NO and $NO_2$; Rappenglück et al., 2000, 2005; Elshorbany et al., 2009a, b).

The most important factor determining surface $O_3$ concentrations in Santiago is the amount of insolation received, as evidenced by the pronounced daily and seasonal $O_3$ cycles (e.g., Gramsch et al., 2006; Schmitz, 2005). On the daily cycle, surface $O_3$ concentrations reach a minimum of 0–5 ppbv at daybreak (0600 local time, hereafter LT) and quickly build during the day, peaking around 1400 LT and then declining again in the evening hours (Elshorbany et al., 2009a; Villena et al., 2011). On the seasonal cycle, $O_3$ concentrations reach a winter minimum (mean daily values less than 20 ppbv) in June and then build to a summer maximum (mean daily greater than 70 ppbv) between July and September (December and March (Gramsch et al., 2006; Elshorbany et al., 2010). Besides the relationship to insolation, other meteorological factors have also been suggested to affect $O_3$ concentrations in Santiago. For example, Rubio et al. (2004) found a positive linear association between maximum $O_3$ levels and maximum local temperature at Las Condes, with ozone exceeding 80 ppbv on 87% of days with temperature above 29 °C but exceeding 80 ppbv on only 16% of days where the temperature did not exceed 29 °C. They speculated that the relationship would be similar across other sites in the city. Rubio et al. (2004) also found that the VOC/NOx ratio (and thus surface $O_3$ concentrations) increased during days with high surface temperature because of an increase in hydrocarbon evaporation and biogenic emissions. Additionally, the diurnal $O_3$ shoulder (slower rate of decline in afternoon $O_3$) has been explained by the favorable predominant afternoon wind direction from the southwest carrying biogenic emissions to the city center (Gramsch et al., 2006). In this study, we will examine these meteorological parameters as they relate to surface $O_3$ variability on the intraseasonal time scale. The remainder of the paper is organized as follows: data and methodology are described in Section 2; intraseasonal variability of $O_3$ and meteorological factors affecting the observed $O_3$ variability are presented in Section 3; and a discussion and conclusions are presented in Section 4.

2. Data and methods

Santiago, Chile, a city with a population of around 6 million, lies in a slightly sloped valley, with a mean elevation of 500 m that rises gradually from its low point in the west to its high point in the east. Further to the east of Santiago rises the Andes Cordillera, with peaks reaching 5500 m. A lower coastal range is located to the west of Santiago with elevations up to 2000 m. Hourly $O_3$ concentration data in ppbv were collected at three observing stations located in the central and eastern side of Santiago (Las Condes, Parque O’Higgins, and Independencia) during the summer months of November–February from Jan 1988–Dec 2010. Four additional stations in Santiago with data records from Jan 1997–Dec 2010 were also examined. Besides $O_3$, all seven of the stations also measured hourly surface wind velocity from Jan 2004–Dec 2011. All data are available publicly from the National Air Quality Information System (SINCA, http://sinca.conama.cl), operated by the Ministry of the Environment. Table 1 summarizes the ozone concentration measurements and Fig. 1 shows the topography of Santiago and the locations of the observing stations; see Gramsch et al. (2006) for a detailed description of each station, including a description of surrounding buildings, roads, and parks.

Phase of the MJO was determined using the Real-time Multi-variate MJO Index (RMM; Wheeler and Hendon, 2004; hereafter WH04). The RMM is based on a pair of principal component time series derived from empirical orthogonal functions of near-equatorially averaged outgoing longwave radiation, 200-hPa zonal wind, and 850-hPa zonal wind. The projection of daily data onto the empirical orthogonal functions acts as an effective time filter and makes the index useful in a real-time setting (WH04). The RMM is divided into eight phases, each corresponding to a broad location of the MJO enhanced convective signal. Active MJO for this study was defined as one where the root sum of the two squared principal components, RMM1 and RMM2, was greater than one. It

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>Mean</th>
<th>Median</th>
<th>Standard Deviation</th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Las Condes</td>
<td>3449</td>
<td>70.9</td>
<td>69.5</td>
<td>44.8</td>
<td>475</td>
<td>0</td>
</tr>
<tr>
<td>Independencia</td>
<td>3522</td>
<td>48.7</td>
<td>46.1</td>
<td>32.0</td>
<td>364</td>
<td>0.048</td>
</tr>
<tr>
<td>Parque O’Higgins</td>
<td>3383</td>
<td>47.0</td>
<td>46.1</td>
<td>26.0</td>
<td>316</td>
<td>0.351</td>
</tr>
</tbody>
</table>
Mean temperature and pressure of the lower-tropospheric inversion were calculated from upper-air observations at SCSN. For each 12Z (0800 LT) sounding, temperature data below 700 hPa was iteratively searched to first identify if a local inversion existed. If one did exist, the data were searched a second, third, and sometimes fourth time to determine whether other inversions existed. If any inversions were found, the inversion with the greatest temperature increase was selected. Inversion temperature change was measured from the point where temperature began to increase to where it began decreasing again, and this temperature change, along with the pressure level of the warmest temperature of the inversion, were used to create the composites.

3. Results

Maximum daily O$_3$ concentrations at Las Condes, Independencia, and Parque O’Higgins (see Fig. 1 for station locations and Table 1 for a summary of descriptive statistics) all showed a distinct pattern of variability with phase of the MJO (Fig. 2). On days when the MJO Index was in Phases 5, 6, and 7, O$_3$ concentrations were high, while on days when the index was in Phases 8, 1, and 2, O$_3$ concentrations were low. Furthermore, the differences in concentrations between Phases 1 and 6 (Phases 1 and 5 at Independencia) were statistically significant at the 95% confidence level for all three stations using the Student’s t-test. While the number of daily observations in each binned phase varied for the three stations, each phase was comprised of between 290 and 375 observations.

Hourly O$_3$ concentrations at each station also showed distinct variability with phase of the MJO (Fig. 3). Ozone concentrations peaked around 1400 LT, with the highest hourly O$_3$ occurring on days when the MJO Index was in Phase 6. Lowest maximum O$_3$ also peaked around 1400 LT and occurred on days when the index was in Phase 1. This result agrees well with the maximum daily concentrations in Fig. 2. All three stations exhibited the same diurnal cycle, with O$_3$ reaching a minimum background value close to 5 ppbv around 0500 LT, increasing rapidly during the morning to 50 ppbv around 1400 LT, then decreasing again in the afternoon with a rapid decline after sunset. The afternoon O$_3$ shoulder, noted by other authors (e.g., Elshorbany et al., 2009b), was visible at both Independencia and Parque O’Higgins, and the hourly O$_3$ values in the shoulder mirror those at the peak: highest O$_3$ during Phase 6, lowest during Phase 1. The shape of the shoulder was the same for all MJO phases.

Fig. 1. Elevation (shaded contours, every 40 m from 400 m to 1600 m) and SINCA station locations (circles). Stations identified by larger circles have data from 1998 to 2010; those at smaller circles have data from 1997 to 2010. Communa political boundaries are in light gray.

Fig. 2. Average maximum daily ozone concentrations by MJO Phase (concentrations in parts per billion, by volume).
Previous authors studying summer O3 in Santiago have found that its concentrations are linked to different meteorological variables, including insolation, surface wind, mixing, surface temperature, and surface dew point temperature. We examined these in turn to test their relationship to intraseasonal O3 variability. The first meteorological variable examined was total cloud cover, which was used as a proxy for insolation. Cloud cover anomalies agreed well with the observed ozone-MJO variability: during MJO Phases 8, 1, and 2, cloud cover was anomalously high, while during MJO Phases 5 and 6, cloud cover was anomalously low (Fig. 4). Considering that normal summer insolation is already high in Santiago, anomalously low (high) cloud cover would thus allow more (less) ultraviolet radiation to reach the surface and allow more (fewer) ozone-producing photochemical reactions. Of the meteorological variables examined in this study, cloud cover anomalies agreed best with the O3 observations.

The second meteorological parameter examined, sea level pressure anomalies, also exhibited significant variability by MJO Phase. Low (high) sea level pressure anomalies were centered about 2000 km southwest of Santiago near 45°S, 90°W during MJO Phase 1 (Phase 6; see Fig. 5). Similarly, weak high (low) sea level pressure anomalies were centered along the central and north-central Chilean coast during Phase 1 (Phase 6). Corresponding surface wind anomalies accompanied the sea level pressure anomalies, with northerly surface wind anomalies occurring during Phase 1 and southerly anomalies during Phase 6. Both the sea level pressure and surface wind anomalies agreed well with the phases of lowest and highest surface O3, with the lowest O3 occurring during Phase 1 and highest during Phase 6.

Next, tropospheric temperatures were examined along a cross-section at 33°S, the latitude of Santiago. Temperature anomalies also varied by MJO Phase, with the strongest contrast in lower-troposphere (surface to 700 hPa) temperatures found between Phases 1 and 6 (Fig. 6). For days when the MJO Index was in Phase 1 (during which O3 was lowest), neutral surface temperatures near and west of Santiago (from 70°W to 75°W) turned to cold anomalies near 850 hPa. The pattern reversed on days when the MJO Index was in Phase 6 (during which O3 was highest), with warm surface temperatures transitioning to even warmer temperature anomalies near 850 hPa. Cold temperature anomalies throughout the lower-troposphere were observed in Phases 2 and 3, and warm anomalies were observed in Phases 7 and 8. These anomalies mapped onto the existing thermal profile of central Chile, which is often characterized by a lower-troposphere morning temperature inversion (Garreaud and Muñoz, 2005).

The vertical profiles of temperature (Fig. 6) suggested weaker temperature inversions on days when the MJO Index was in Phase 1 and stronger temperature inversions on days when the index was in Phase 6. To test this hypothesis, 12Z sounding data were examined from the regular upper-air station at Santo Domingo (along the coast approximately 90 km west-southwest of Santiago). During Phases 1 and 2, inversion strength (measured by the change in temperature from the base to the top of the inversion) was lowest, around 5–5.5 °C (Fig. 7). During Phases 6, 7, and 8, inversion strength was highest, between 7 and 7.5 °C. Inversion pressure levels (the pressure level of the base of the inversion) were highest (farthest from the ground) during Phases 7, 8, 1, and 2 and lowest (closest to the ground) during Phases 3, 4, and 5. These data were roughly in agreement with the temperature cross-sections, and indicated that MJO Phases with colder (warmer) lower-troposphere temperatures and weaker (stronger) low-level temperature inversions roughly corresponded to MJO Phases with lower (higher) surface O3. These differences between phases, however, were not statistically significant at the 95% confidence level.

In addition to the radiosonde data, morning, noon, and afternoon (0600, 1200, and 1800 LT) surface conditions at the Santiago International Airport (SCEL) were also examined. Greatest variability by phase of the MJO was found in sea level pressure, with low sea level pressures occurring during Phases 5, 6, and 7 and high pressures during Phases 1 and 2 (Fig. 8), in good agreement with the reanalysis sea level pressure pattern (Fig. 5). The variability in sea level pressure, along with the cloud cover anomalies in Fig. 4, agree with the findings of Rutllant and Garreaud (1995), who noted that clear skies in central Chile were most often associated with a coastal pressure trough. Furthermore, the difference in sea level pressure between Phases 2 and 6 was statistically significant at the

\[ \text{Fig. 3. Diurnal cycle of ozone concentration (pptv) at Las Condes, Independencia, and Parque O'Higgins, 1988–2010, by MJO Phase. Phases 1 and 6 indicated by circles and squares, respectively.} \]
95% confidence level. Morning, noon, and afternoon cloud ceiling heights, which we considered as another approximation for isolation, were highest during Phases 5 and 6, and lowest during Phases 8, 1, and 2, again in rough agreement with the phases with high (Phases 5 and 6) and low (Phases 1 and 2) O₃.

Not all of the meteorological parameters at SCEL showed as much variability between MJO Phases as cloud cover, sea level pressure, and ceiling height. Noon and afternoon surface temperature anomalies, which were lowest during Phases 1 and 2, were only neutral to slightly positive during MJO Phases 5 and 6 and highest in Phases 7 and 8. Noon dew point temperature anomalies were lowest in Phases 5 and 6 and highest in Phases 8, 1, and 2; however, the anomalies were not large. Wind speed anomalies, noted in earlier studies as possibly being responsible for the afternoon O₃ shoulder at Parque O’Higgins and Independencia, were highest in Phases 8 and 1, neutral in Phases 5 and 6, and lowest in Phase 4. However, wind velocity, both speed and direction, at each SINCA station did not change significantly between MJO Phases 1 and 6 (Fig. 9).

4. Discussion and conclusions

Surface ozone has been the subject of many studies in Santiago and other global cities. However, few (if any) studies exist that have examined its intraseasonal variability or connection to phase of the MJO. The results presented here confirm that for the Santiago metropolitan region, both maximum daily O₃ concentrations as well as the diurnal cycle of O₃ varied by MJO Phase, with lowest O₃ occurring on days with the MJO Index in Phases 1 and 2 and highest O₃ occurring on days with the MJO Index in Phases 5 and 6. Additionally, the difference between the lowest (Phase 1) and highest (Phase 6) concentrations was statistically significant at the 95% confidence level. Composite anomalies of total cloud cover were in good agreement with the O₃ data, with highest (lowest) cloud cover anomalies occurring in the phases with highest (lowest) surface O₃ concentrations. Sea level pressure and surface wind anomalies provided supporting evidence for a meteorological explanation for the observed O₃ anomalies, with a surface pressure trough (ridge) located along the Chilean coast during phases of high (low) cloud cover and O₃. Surface data at Santiago International Airport varied by phase of the MJO, with highest (lowest) surface pressures occurring during periods of low (high) O₃, a result that is statistically significant at the 95% confidence level. These results are both in good agreement with each other, suggesting that anomalously low sea level pressures and clear skies are associated with higher O₃ concentrations.

Surface temperature and ceiling height were somewhat in agreement with O₃ concentrations, with higher (lower) temperature and ceiling anomalies mostly occurring during phases with high (low) O₃ concentrations, but the variability was not statistically significant. Wind velocities over Santiago showed little change between Phases 1 and 6. Lower-tropospheric temperature anomalies over and upstream of Santiago were found to reverse signs, depending on MJO Phase: cold anomalies occurred during Phase 1, warm anomalies occurred during Phase 6, suggesting a modulation of the temperature inversion by the MJO. Indeed, data from the nearest regular upper-air station show weaker (stronger) and higher (lower) above-ground temperature inversions during the low (high) ozone phases, although like the surface data from the airport, the signal was not as pronounced as that found in either
cloud cover anomalies or sea level pressure. These results agree with Berman et al. (1999), who suggested that a relationship existed between morning inversion height and strength and summer O₃ in Houston. However, the relationship between surface O₃ and low-level temperature inversions remains unclear, as Rappenglück et al. (2008) found essentially the opposite result, and Banta et al. (2011) found that neither boundary layer depth nor maximum surface temperature affected surface O₃ in Houston, but rather lower-troposphere wind direction.

For Santiago, we found the greatest intraseasonal relationship between O₃ and cloud cover, with secondary agreement with surface and lower-troposphere temperature. Because cloud cover...
in Santiago is often related to the strength and height of the lower-troposphere temperature inversion (e.g., Rutllant and Garreaud, 1995), the amount of influence that inversion strength and height would have on O₃ would depend on how much the inversion affected insolation and diurnal mixing of morning stratus. In this study, those variables were not examined in depth due to lack of upper-air observations over Santiago. Also, it is important to note that the radiosonde data used in this study were collected at sea level along the coast 90 km west-southwest of Santiago, thereby sampling a more marine environment than that characteristic of Santiago. Thus, additional research — particularly research that incorporates upper-air information from the air column above Santiago — is needed to further solidify the relationship between the lower-tropospheric temperature and surface O₃.

Finally, it is important to note that O₃ variability by MJO Phase for the other four SINCA stations (with data from 1997 to 2010) resembled the pattern in Fig. 3 for MJO Phases 1 to 7. However, O₃ concentrations in Phase 8 behaved differently from those at Las Condes, Independencia, and Parque O’Higgins, increasing during Phase 8 rather than decreasing. Additionally, when the 1997–2010 record was isolated for all seven stations, the anomalous increase at Phase 8 was seen at all locations. While several factors may explain this anomaly, including lack of sufficiently long data records to capture multiple cycles of the MJO, additional research is needed to determine whether a material change in the relationship to the MJO has occurred for Phase 8 in recent years.

Acknowledgments

We would like to thank the U.S. Naval Academy Research Council (NARC) for financial support for this investigation. Additionally, NCEP Reanalysis 2 data was provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/. We also thank two anonymous reviewers for their helpful comments to improve the manuscript.