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# Day-of-Week Patterns in Diurnal Profiles of $NO_2$/NO Ratios Los Angeles Area, 1989 through 1998

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## Introduction

In support of our ongoing analysis of weekday-weekend differences in air pollution, we computed diurnal profiles of $NO_2$/NO ratios for sites in California's South Coast Air Basin. $NO_2$/NO ratios provide information about conditions for ozone formation, and generally rise and fall roughly in step with ozone concentration. We constructed profiles for all seven days, for each site, then examined the profiles to determine whether patterns exist among sites. This document is a preliminary summary of findings. It presents descriptive information only, pending further analysis. We do not enter into interpretation or explanation because we believe the data presented here must be interpreted in the context of other data, such as volatile organic compound and organic radical concentrations, which are still undergoing analysis.

## Data

Data consisted of hourly average $NO_2$ and NO concentrations for 22 sites in the South Coast Basin, for May through October, 1994 and 1998. The years were chosen to represent conditions before and after the introduction of California Cleaner Burning Gasoline in 1996. Data were taken from the ADAM database, the ARB's repository for criteria air pollution data. For information on this dataset, and for data requests, please see the ARB Air Quality web site: http://www.arb.ca.gov/aqd/aqd.htm.

## Methodology

Prior to taking averages, we transformed the data according to the relationship $y = \log( x + 0.5\ ppb )$ to guard against zeroes and small values in the denominator of the ratio. The offset of 0.5 ppb represents 1/2 the lower limit of detection (LOD) of the analytical method for NO and $NO_2$ . By adding this offset, we reduced the variability of the ratios considerably at the cost of a slight bias towards lower ratios. We computed mean differences of the transformed concentrations by site, year, day of week and hour of day, then back-transformed by exponentiating. The resulting means are therefore close to the geometric means.

For each site, for each of the two years, we plotted profiles (mean hourly concentration plotted against time of day) for all seven days superimposed. We also plotted and examined individual daily profiles for outliers, to ensure that the average diurnal profiles were not unduly influenced by anomalous observations Each profile represents roughly 26 days of data.

The descriptions below are an attempt to characterize overall patterns common to multiple sites. A given site, in a given year, may lack some of the characteristics described.

## Results

### Overall Patterns

- $NO_2$/NO ratio diurnal profiles resemble ozone profiles in having a midday peak. The ratio climbs sharply starting around 7-8 AM PST, and peaks around noon. Most profiles show a second cusp around 6 PM, frequently slightly higher than the midday peak. After 7 PM, concentrations generally decrease until reaching a minimum at 6 AM the next morning (Figure 1)
- Site by site, peak ratios range from around 2 to 30, with 10-15 being typical (Figures 1, 2, 5). West-side sites (Hawthorne, Costa Mesa, La Habra, Lynwood, Long Beach) are generally low. The peak ratio at Lynwood in 1998, in particular, is extremely low relative to other sites (Figure 6). No strong pattern is evident among sites with high peak ratios.
- At almost every site, Sunday $NO_2$/NO ratios are markedly higher than other days around 6-9 AM. Saturday 6-9 AM concentrations are generally higher than weekdays but lower than Sunday (Figures 1, 2). Morning NO and $NO_2$ absolute concentrations are generally lowest, by a considerable margin, on Sunday, with Saturday concentrations intermediate between Sunday and weekdays (Figures 3, 4). The high $NO_2$/NO ratios concentrations on weekends are due mainly to the sharp drop in morning NO.
- Riverside and San Bernardino area sites generally show a skewed shape with a rapid AM climb followed by a gradual build-up until evening (Figure 5).

**Differences between 1994 and 1998**

- Most sites show an increase of 50-100% in peak ratios from 1994 to 1998 (Figures 1, 2), although a few sites decrease by as much as 20%. This is mainly due to a drop in afternoon and evening NO concentrations in 1998. Afternoon NO concentrations tend to be close to LOD.
- At some sites (Azusa, Hawthorne, Pico Rivera, LA, Riverside, S. Bernardino) the evening $NO_2$/NO ratio peak is markedly higher than the AM peak in 1998 (Figure 2). This is mainly because evening NO concentrations are extremely low, while $NO_2$ concentrations are relatively high.
- In 1994, about one-fourth of the sites show a "Sunday afternoon trough", with Sunday $NO_2$/NO ratios lower than other days of the week from around 12-6 PM (Figure 5). This is less evident in 1998.
- In 1994, the $NO_2$/NO 12-5 AM ratios are highest on Monday at most sites. This is not evident in 1998 (Figures 1, 2)
- In 1994, Friday has the lowest $NO_2$/NO ratio from 6-9 AM at most sites (Figure 5; while the difference between Friday and other weekdays is small, the pattern is consistent among almost all sites). This is not evident in 1998. However, in 1998, Friday NO/ $NO_2$ ratios are the lowest in the week from 5-11 PM at about half the sites (Figure 2).

**Discussion**

We present this preliminary information for the purpose of discussion, in the hope that it will suggest directions for continued research.

A word of caution is in order about interpreting $NO_2$/NO ratios. While the $NO_2$/NO ratio reflects the conversion rate of NO to $NO_2$, it is also affected by losses of both species due to deposition, reaction, etc. $NO_2$/NO ratios, by themselves, are generally not considered a reliable indicator of radical formation or ozone formation rate. Moreover, since $NO_2$ is computed by subtracting a directly measured NO concentration from a directly measured NOx concentration, and NOx measurements are affected by the presence of nitric acid and other species, there is considerable measurement uncertainty. This is particularly true of afternoon NO concentrations, which approach the lower sensitivity limit of the measuring instrument. While due care was taken in the statistical analysis to minimize the impact of low NO concentrations, more investigation into the effect of measurement interferences upon $NO_2$/NO ratios is needed.

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**Figure 1**

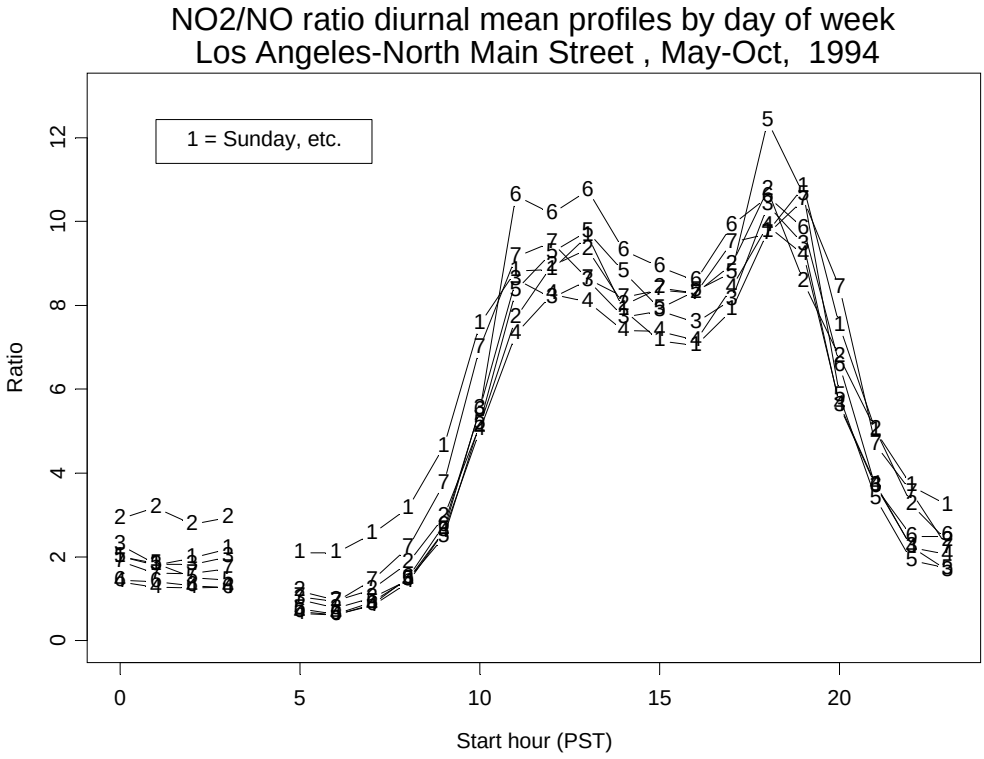


**Figure 2**

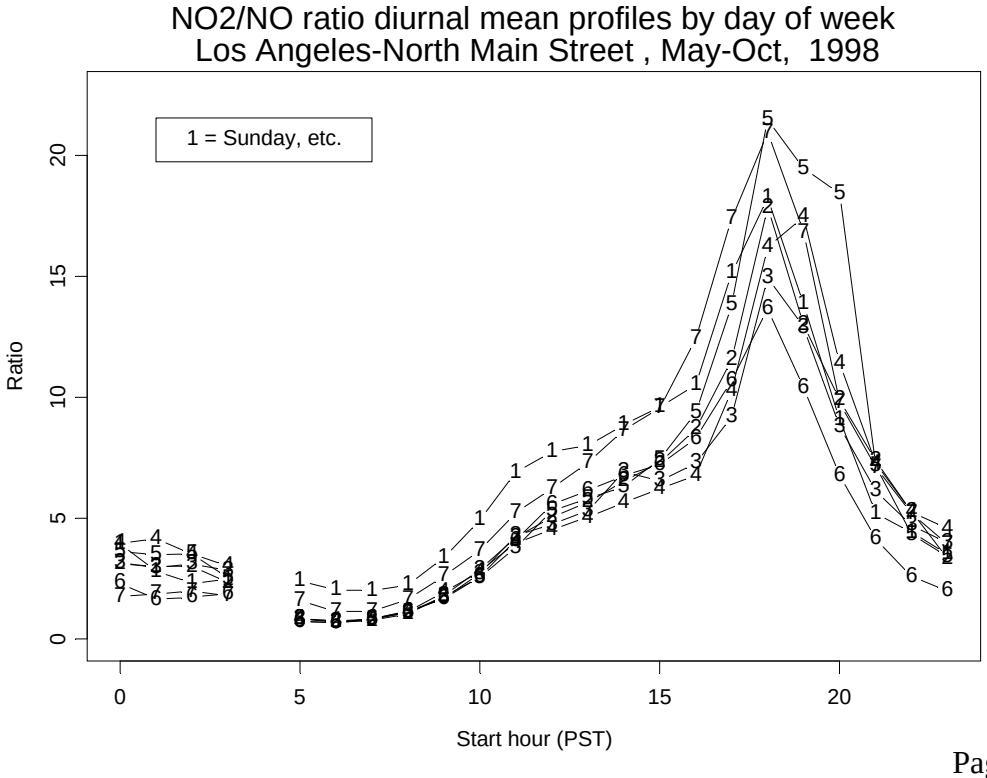

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**Figure 3**

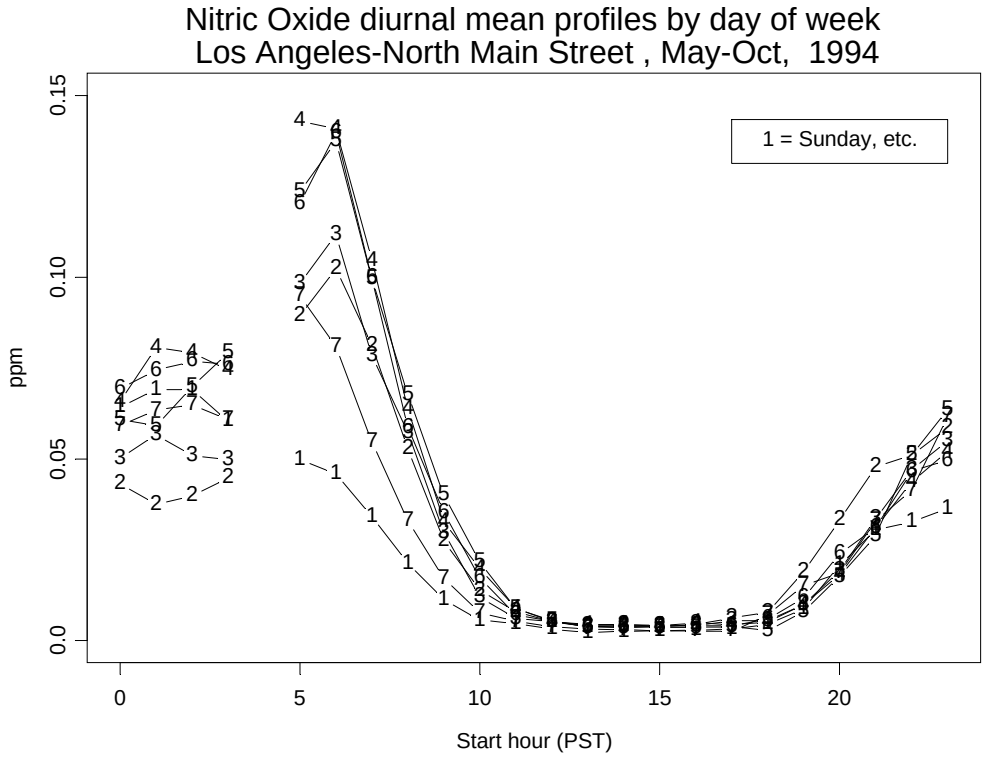


**Figure 4**

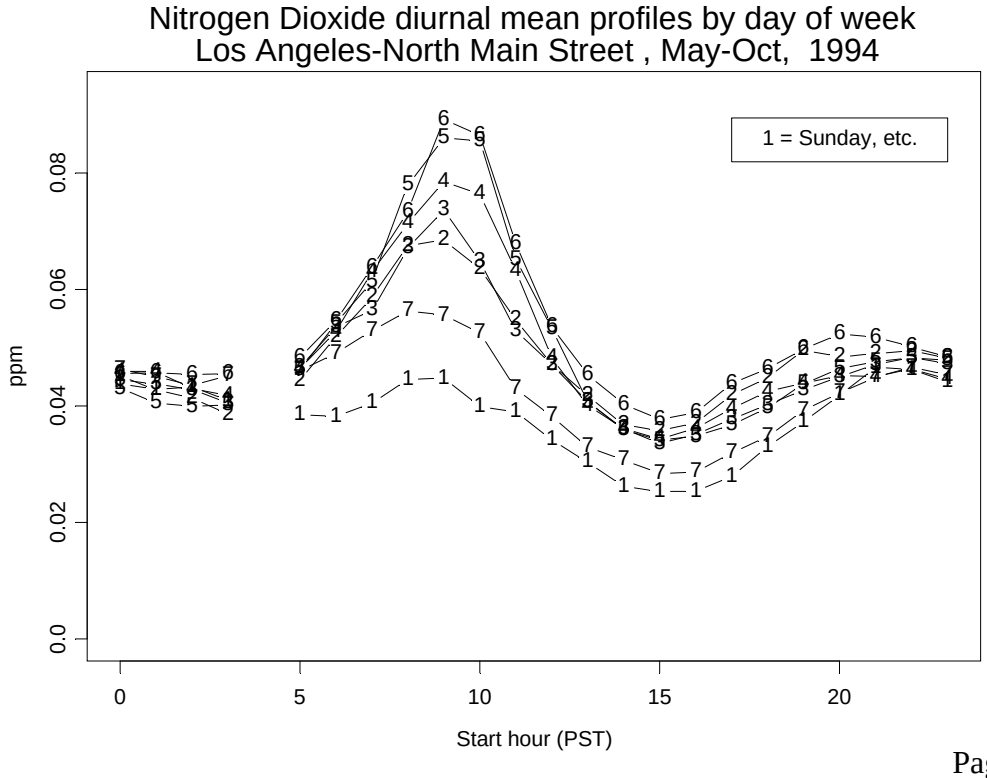

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Figure 5

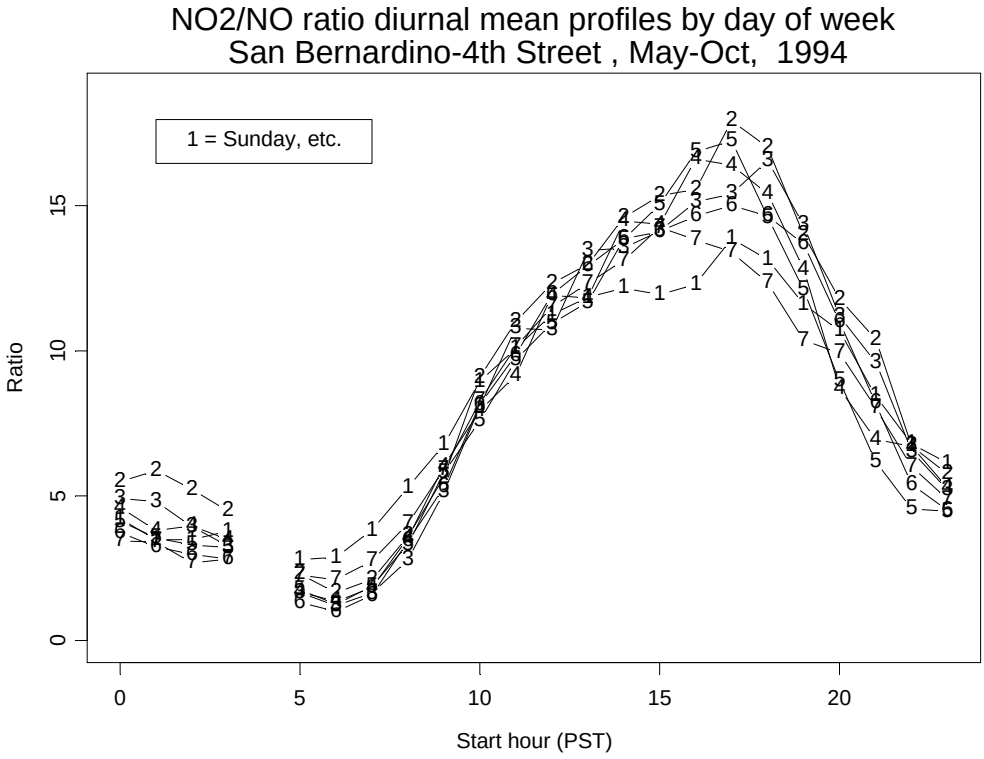


**Figure 6**