

TRENDS IN AMBIENT NO_x AND PARTICULATE NITRATE CONCENTRATIONS IN CALIFORNIA, 1980-2000

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SUMMARY

Trends in monthly-average oxides of nitrogen (NO_x), particulate matter less than 10 micrometer (μm) aerodynamic diameter (PM_{10}) mass, PM_{10} nitrate, total suspended particulate (TSP) mass, and TSP nitrate concentrations were analyzed for each monitoring location in the South Coast, South Central Coast, and Mojave Desert air basins for the period 1980-2000. In addition, trends in monthly-average NO_x , PM_{10} mass, TSP mass, PM_{10} nitrate, and TSP nitrate concentrations were studied in relation to trends in temperature, precipitation, and primary pollutant levels at seven long-term (10 years or more) monitoring sites in the South Coast, San Joaquin Valley, and San Francisco Bay Area air basins for the period 1980-2000 using stepwise multiple regression. The sites were Azusa, Fremont, Livermore, Napa, Riverside, San Bernardino, and Visalia. Since the time resolution and frequency of sampling varied among compounds, measurements were recompiled as monthly averages prior to analyzing for trends. Measurement biases associated with the available monitoring data limit the reliability of some of the trend assessments, as discussed in the report.

From 1980 to 2000, ambient PM_{10} nitrate concentrations decreased at faster rates than did ambient NO_x concentrations at the majority of the California monitoring locations studied. At monitoring sites in the South Coast, South Central Coast, and Mojave Desert air basins, the mean rate of decline of monthly-average PM_{10} nitrate concentrations was 0.304 percent per month (mean S.E. 0.109 percent per month), whereas the mean rate of decline of monthly-average NO_x was 0.080 percent per month (mean S.E. 0.080 percent per month). The ambient NO_x declines tended to be greater near the coast, whereas the PM_{10} nitrate declines tended to be greater in the northern South Coast Air Basin and north of the basin. Of 16 southern California sites with both NO_x and PM_{10} measurements, five showed opposite trends in NO_x and PM_{10} nitrate concentrations (2 had increasing PM_{10} nitrate with decreasing NO_x , while three had decreasing PM_{10} nitrate with increasing NO_x). Six sites showed trends in PM_{10} nitrate and NO_x that were directionally the same but differed in magnitude by factors of two to four (4 sites with greater trends in PM_{10} nitrate than in NO_x). Five sites (Anaheim, Azusa, Burbank, San Bernardino, and Santa Clarita) showed quantitatively similar trends for NO_x and PM_{10} nitrate. Decreasing trends

were evident for all compounds studied at the majority of monitoring sites in the South Coast, South Central Coast, and Mojave Desert air basins: PM₁₀ mass (50 of 53 sites declined, with 37 declines statistically significant), NO_x (34 of 48 sites declined, with 25 declines statistically significant), PM₁₀ nitrate (20 of 25 sites declined, with 12 declines statistically significant), and TSP nitrate (25 of 38 sites declined, with 13 declines statistically significant).

At the seven long-term monitoring sites whose data were studied in more detail, the trends in PM₁₀ nitrate also exceeded trends in NO_x: as determined from simple regressions of concentration against time, the median NO_x trend at these seven sites was a decline of 1.3 percent per year, whereas the median PM₁₀ nitrate trend was a decline of 3.6 percent per year. As determined from stepwise multiple regressions that included the effects of temperature and precipitation, the median NO_x trend was a decline of 1.4 percent per year, whereas the median PM₁₀ nitrate trend was a decline of 3.1 percent per year. These differences indicate that declining NO_x levels alone were not responsible for declining nitrate concentrations, because PM₁₀ nitrate is not expected to exhibit a greater than proportional response to changing NO_x levels.

The stepwise multiple regressions confirmed the trends estimated from the simple regressions. The median trends in NO_x, 1.3 percent per year for the simple regressions and 1.4 percent per year for the multiple regressions, agreed closely. For PM₁₀ mass, the median trend was 3.3 percent per year for the simple regressions and 3.7 percent per year for the multiple regressions. For PM₁₀ nitrate, the median trend was a decline of 3.6 percent per year for the simple regressions and 3.1 percent per year for the multiple regressions. Trends in NO_x, PM₁₀ mass, TSP mass, PM₁₀ nitrate, and TSP nitrate occurred during both warm and cool seasons.

Monthly average concentrations of NO_x, PM₁₀ mass, TSP mass, PM₁₀ nitrate, and TSP nitrate all varied inversely with precipitation amount. NO_x, PM₁₀ mass, and TSP mass varied directly with temperature at 4 of the 7 sites. When PM₁₀ nitrate and TSP nitrate varied with temperature, the relationship was inverse for PM₁₀ nitrate but direct for TSP nitrate. Temperature and precipitation trends contributed to the trends in PM₁₀ nitrate and TSP nitrate.

Inclusion of ambient NO_x , carbon monoxide (CO), and coefficient of haze (CoH) concentrations in addition to temperature and precipitation in the statistical models accounted for the PM_{10} nitrate trends, since PM_{10} nitrate levels showed no trend beyond that which was related to changes in ambient NO_x , CO, and CoH concentrations, temperature, and precipitation. Thus, nitrate levels have responded to primary pollutant changes. But because the magnitudes of the NO_x trends alone were insufficient to account for the nitrate trends, it is likely that ambient nitrate levels have responded to reductions of primary pollutants in addition to NO_x . The regressions linked PM_{10} nitrate and TSP nitrate to NO_x , but also to CO or CoH at some sites. The measurements do not permit more specific determination of the effects of each primary pollutant on ambient PM_{10} nitrate or TSP nitrate.

In comparison, analyses of the weekend effect in southern California have shown that weekend NO_x levels are significantly lower than weekday levels, but no statistically significant differences exist between weekday and weekend levels of $\text{PM}_{2.5}$ nitrate, PM_{10} nitrate, or TSP nitrate (Blanchard and Tanenbaum, 2003). Compared with weekdays, weekends show a much stronger reduction of ambient NO_x levels than of ambient hydrocarbon concentrations (Chinkin et al., 2003). The weekend emission pattern thus differs from the historical record, which shows strong reductions of all primary pollutant levels. The absence of nitrate reductions on weekends in response to lowered NO_x levels suggests that the historical nitrate trends are related in part to reductions of primary pollutants in addition to NO_x .

Primary PM_{10} mass was estimated as: primary mass = mass-sulfate- nitrate- ammonium. At the seven long-term sites, the estimated primary TSP mass declined by 1.9 to 3.0 percent per year, and the estimated primary PM_{10} mass declined by 2.4 to 4.8 percent per year. In contrast, inventory primary PM_{10} emissions show no decline. This discrepancy warrants further analysis.

The present study does not evaluate the consistency of trends in estimated primary pollutant emissions and ambient concentrations at the full set of California monitors. Additional efforts are needed to further clarify how PM_{10} nitrate and $\text{PM}_{2.5}$ nitrate levels have responded to emission changes throughout California.

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1. INTRODUCTION

The Importance of Particulate Nitrate in California

The average composition of fine particles varies considerably across North America (NARSTO, 2002). In California, particulate nitrate concentrations represent over one-quarter of the average annual fine mass at both urban and rural monitoring sites (Chow et al., 1993; Christoforou et al., 2000; Chow et al., 1999). At sites in California's San Joaquin Valley, nitrate accounts for ~30 percent of the annual-average fine particle mass (Chow et al., 1993; Chow et al., 1999). In Los Angeles, nitrate also accounts for ~30 percent of the annual-average fine particle mass at sites in the western and central portions of the basin, but this fraction increases to ~40 percent in the eastern basin (Motallebi et al., 2003a). Annual-average fine-particulate nitrate concentrations in the San Joaquin Valley and the Los Angeles area range from about 6 to 16 $\mu\text{g m}^{-3}$, with daily-average nitrate levels reaching as high as 100 $\mu\text{g m}^{-3}$ on some days in the eastern Los Angeles basin. The ammonium associated with nitrate typically accounts for ~10 to 20 percent of the annual-average fine particle mass in the San Joaquin Valley and southern California (Motallebi et al., 2003a). In some locations, therefore, ammonium nitrate levels alone suffice to cause violations of the 15 $\mu\text{g m}^{-3}$ annual-average national fine-particle standard.

Particulate nitrate derives partially or predominantly from the equilibrium reaction between two gas-phase species, nitric acid and ammonia. The equilibrium favors the condensed phase at lower temperatures and higher humidities, so particulate nitrate concentrations are generally higher during winter months. Reaction of nitric acid with sea salt aerosol is another pathway for the production of particulate nitrate. Nitric acid (HNO_3), in turn, derives from oxidation of NO_2 . During the day, nitric acid is produced by reaction of NO_2 with the OH radical. Different reaction pathways predominate during the night compared with the day; however, measurements often indicate that nighttime concentrations of nitric acid are below detection limits.

The reaction of ammonia with nitric acid is affected by the amount of sulfate present. Ammonia reacts preferentially with sulfuric acid, and, if sufficient ammonia is available, it then

combines with nitric acid to form particulate nitrate. In California, particulate sulfate concentrations are typically lower than in many other parts of the country (NARSTO, 2002), and sufficient ammonia is available at most times and locations to allow the formation of particulate ammonium nitrate (Blanchard et al., 2000). In contrast, the availability of ammonia limits particulate nitrate formation during most times at sites in the southeastern United States (Blanchard and Hidy, 2003).

Since the availability of ammonia typically does not limit the amount of particulate nitrate occurring at most California locations, the amount of particulate nitrate that forms depends upon the amount of nitric acid. This amount in turn depends upon the rate of conversion of NO_2 to nitric acid. During winter in the San Joaquin Valley, NO_2 concentrations typically exceed concentrations of nitric acid (Kumar et al., 1998), implying that the rate of conversion of NO_2 to nitric acid is a key determinant of ambient concentrations of nitric acid, and, hence, of particulate nitrate levels. Initial modeling efforts suggest that in one of the urban areas of the San Joaquin Valley, nitric acid formation is limited by the availability of radical species, and particulate nitrate formation may be more effectively reduced through reductions of VOC than NO_x emissions (Pun and Seigneur, 2001). Outside the urban areas, however, nitric acid formation in the San Joaquin Valley may be responsive to changes in NO_x emissions (Stockwell et al., 2000), especially over multiday stagnation episodes. These findings have significant implications for the control of PM, and additional research efforts are needed to fully understand the implications. The present project is intended to provide an empirical assessment of the responsiveness of particulate nitrate concentrations to changes in NO_x levels using available databases.

Trend Assessment

Comparing emission changes with changes in ambient air pollutant concentrations potentially provides information on the effectiveness of emission control programs, including the present question of the relation of changes in NO_x levels to changes in particulate nitrate concentrations. However, emissions-related trends (the signal of interest) in ambient concentrations are difficult to quantify because the majority of the day-to-day, and even year-to-year, variation in concentrations is typically attributable to variations in weather (noise). Where

a data record exists that is long enough to support trend assessments (typically decadal), characterization of trends provides an important technique for evaluating the success of ongoing control programs (NARSTO, 2002).

The detectability and quantifiability of trends in ambient pollutant concentrations depends upon the magnitudes of emission reductions or increases, the quality and length of record of the monitoring data, and the relative magnitudes of the emissions-related (signal) and weather-driven (noise) variations in ambient pollutant concentrations (NARSTO, 2002). For a signal-to-noise ratio of 1:1, about two to four years of monthly data are typically needed to detect a linear trend with high probability (90 percent) at a 95 percent confidence level, whereas 10 to 20 years of data are generally needed when the signal-to-noise ratio falls to 0.1:1 (Weatherhead et al., 1998). The latter, low signal-to-noise ratio, is usually characteristic of ambient pollutant measurements.

Many of the existing analyses of PM or deposition trends suggest that a ten-year record is typically necessary for detecting changes on the order of ten to twenty percent of the measured concentrations. Indeed, some of the more sophisticated trend techniques have shown the existence of three-to-five year cycles in precipitation sulfate concentrations (Sirois, 1993) and in particulate sulfate, nitrate, and ammonium concentrations (Vet et al., 2001). The presence of such multi-year cycles implies that a record of ten years or more is necessary for establishing the existence and significance of long-term trends.

The interpretation of ambient pollutant trends requires careful consideration of all factors that might be affecting the observed trends. These factors include variations in emissions of precursors, atmospheric reactions affecting the conversion of primary to secondary pollutants, and changes in meteorological conditions over the time periods of interest.

National and California Particulate Matter Trends

Many sites in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network have shown declining PM_{2.5} mass concentrations over the 11-year period from 1988 through 1998 (Figure 1). In California, median fine mass concentrations declined at

four IMPROVE sites (Redwood National Park, Point Reyes, Pinnacles, and San Geronio Wilderness), but showed no trend at Lassen and Yosemite National Parks. On the worst 20 percent of the days, fine mass concentrations increased over the same period at Yosemite and Lassen, showed no trend at Redwood, and declined at the remaining three locations (Malm, 2000). The possible influence of meteorological cycles is suggested by the presence of statistically significant trends at Point Reyes National Seashore and Redwood National Park, two locations on the Pacific Coast that are minimally influenced by emissions from sources within California.

In eastern North America, a pronounced decrease of particulate sulfate concentrations occurred during the 1990s (Schreffler and Barnes, 1996; Shannon, 1999), related in part to the U.S. Phase I SO₂ emission controls that were implemented as of the end of 1994 (Figure 2). Particulate nitrate concentrations exhibited little or no change during the same time period (Figure 2). According to the U.S. EPA, nationwide SO₂ emissions declined by 35 percent from 1992 to 2001, whereas NO_x emissions declined by only three percent during the same period (U.S. EPA, 2002). Thus, the differences in the trends in particulate sulfate and nitrate are potentially related to differences in the trends of their gas-phase emissions precursors.

For secondary pollutants, such as particulate sulfate and nitrate, air-quality trends may or may not follow the trends exhibited by precursor emissions, because secondary pollutant formation depends also upon the rates of conversion of precursor to secondary species. As previously noted, the formation of particulate nitrate typically occurs as a temperature- and humidity-dependent equilibrium reaction between gas-phase ammonia and nitric acid, so that nitrate levels in some locations may depend upon the availability of ammonia. Moreover, the rate of formation of nitric acid from NO₂ depends upon radical species (see Section 2). Therefore, one-to-one correspondence between NO_x and particulate nitrate trends is not to be expected.

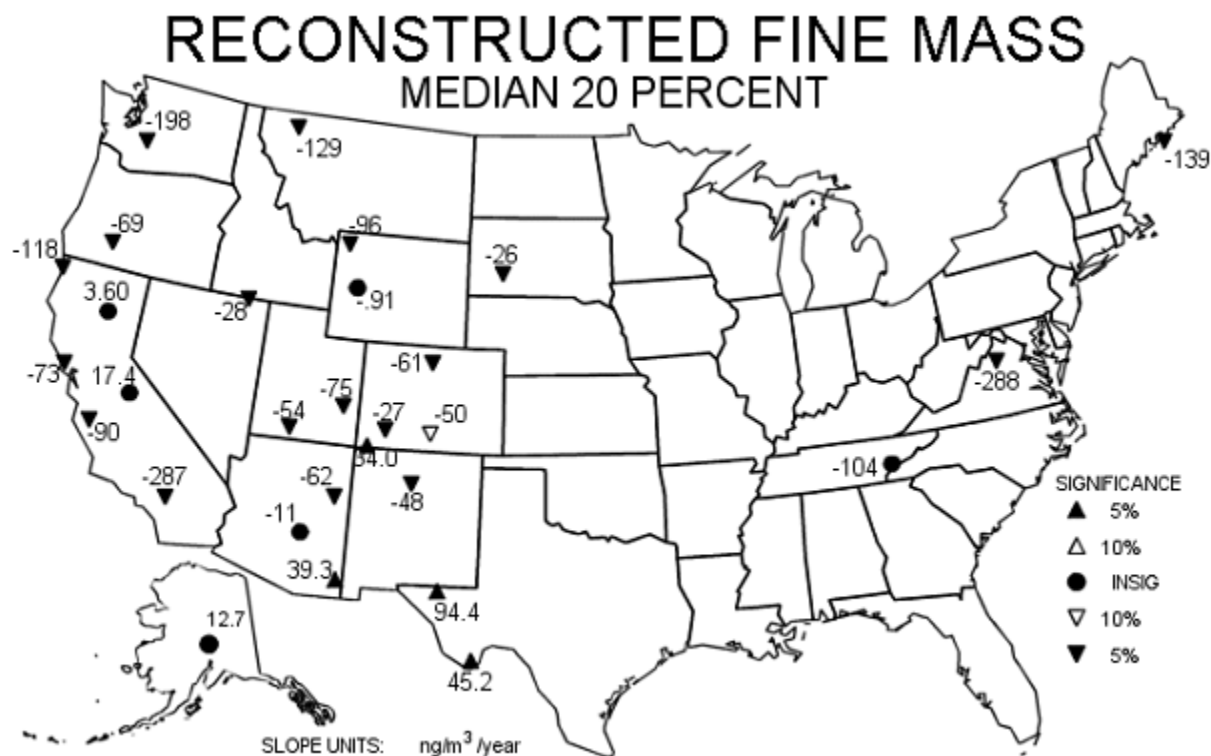


Figure 1. Trends in median $\text{PM}_{2.5}$ mass at IMPROVE sites, 1988-98. Arrows denote upward or downward trends. Solid arrows indicate significance at $p < 0.05$ while open arrows indicate significance in the range of $0.05 < p < 0.10$. (Source: Malm, 2000).

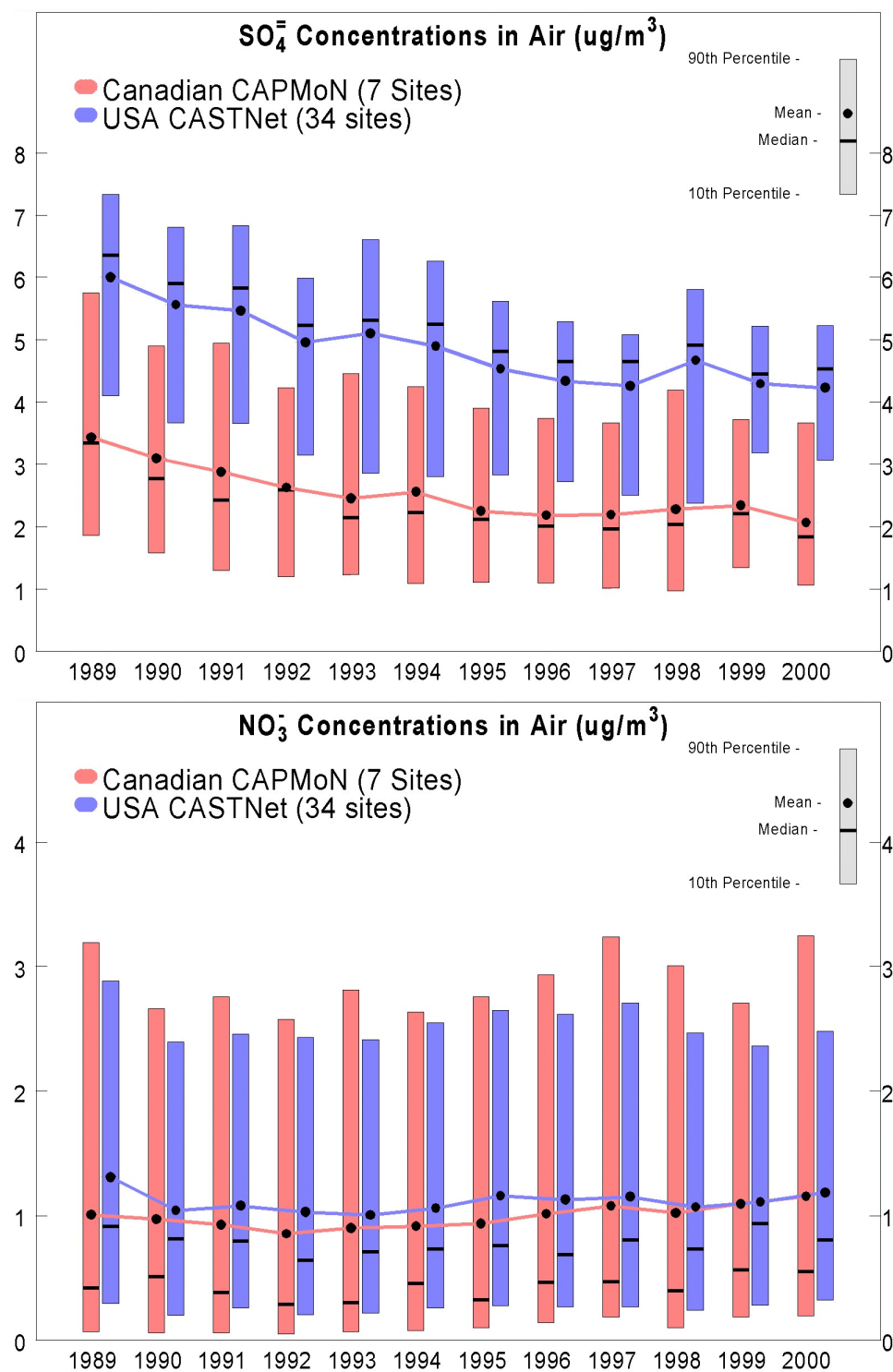


Figure 2. Trends in annual particulate sulfate (top) and nitrate (bottom) concentrations based on 34 U.S. CASTNet and 7 Canadian CAPMoN sites. Shown are boxplots of annual mean, median and 10th and 90th percentile concentrations for the combined sites. (Source: NARSTO, 2002).

In California, past trends in particulate sulfate levels are noteworthy for two reasons. First, such trends have led to present-day conditions, with low ambient levels of sulfate and SO₂. Second, sulfate trends provide an example of a nonproportional response to changes in precursor emissions. Substantial changes in particulate sulfate levels occurred in California beginning in the late 1970s. In Los Angeles, SO₂ emissions varied from about 250 to 350 tons per day during the years from 1970 to 1977, and decreased to about 265 tons per day in 1979 and 150 tons per day by 1983 as power plants switched from oil to natural gas beginning in 1978 (Hidy, 1994; Alexis et al., 2001). SO₂ emissions further declined to about 120 tons per day in 1987, following the introduction of low-sulfur gasoline in 1983, and to about 77 tons per day by 1996 with continuing adoption of other control measures. During the period from 1976 to 1996, annual-average SO₂ concentrations in the Los Angeles area declined by over 70 percent, which corresponds closely with the 71 percent decrease in SO₂ emissions from 1979 to 1996. Annual-average sulfate concentrations declined by about 50 percent from 1976 to 1996 (Hidy, 1994; Christoforou et al., 2000), although a greater decline may have occurred in non-seasalt sulfate. The decline in sulfate concentrations lagged the SO₂ concentration decline by about five years, and did not become apparent until the ambient SO₂ concentrations had been reduced by over 40 percent. Current scientific understanding indicates that the time lag and nonproportional decline of sulfate concentrations occurred because the conversion of SO₂ to sulfate was oxidant-limited; no other explanations are known.

During more recent years in the South Coast Air Basin, the maximum annual PM₁₀ mass, sulfate, and nitrate concentrations declined by 36 percent, 16 percent, and 24 percent, respectively, between 1988 and 1995 (Dolislager and Motallebi, 1999). In the San Joaquin Valley, the maximum annual PM₁₀ mass, sulfate, and nitrate concentrations declined by 27 percent, 50 percent, and 34 percent, respectively, between 1988 and 1995 (Dolislager and Motallebi, 1999). At North Long Beach and Riverside, the trends in ambient NO_x and TSP¹ nitrate levels from 1978 to 1995 were closely parallel, whereas the TSP sulfate levels declined more slowly than did ambient SO₂ concentrations (Dolislager and Motallebi, 1999). These

¹Total suspended particulate. The measurement instruments capture particles up to ~ 30 µm aerodynamic diameter.

trends support the interpretation that SO₂ levels were not limiting the formation of total particulate sulfate during those times at those locations, whereas NO_x levels could have been limiting nitrate formation (a corresponding record for fine-particle nitrate extending back to 1978 does not exist).

Annual-average fine-particle levels measured by California's dichotomous sampler network (1988-1999), the California Acid Deposition Monitoring Network (CADMP) (1988-1998), and the Children's Health Study (two-week samplers, 1994-1999) network all showed generally declining levels (Motallebi et al., 2003b). The relations of these trends to emission trends have not been quantified, but are not expected to be one-to-one due to the nonlinear nature of the reactions leading from primary to secondary species (Motallebi et al., 2003b).

Overview of Report

Section 2 of this report provides background information on particulate nitrate formation. In Section 3, we discuss the measurement of particulate nitrate, with emphasis on questions of accuracy. Section 4 discusses the availability of PM measurements in California suitable for analysis for long-term trends in nitrate. Section 5 summarizes previous work by us on PM trends in the South Coast Air Basin (Blanchard and Tanenbaum, 2001). This earlier work includes descriptions of trends at all routine monitoring sites in southern California and serves as a foundation for the statistical analyses that were carried out under the present project. Section 6 describes the methods used for new trend analyses. Section 7 presents the new results. Conclusions are summarized in Section 8.

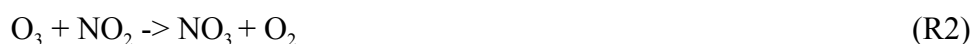
2. BACKGROUND

Particulate Nitrate Formation

Particulate nitrate derives from emissions of nitrogen oxides (NO_x), but in a highly nonlinear manner. Gas-phase oxidation of NO_2 yields nitric acid (HNO_3); aqueous-phase reactions are by comparison unimportant. During daytime, HNO_3 is produced by reaction of NO_2 with hydroxyl radical (OH):

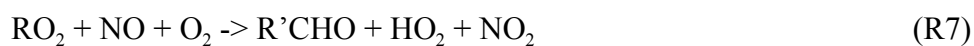


At night, the following reactions become more important than (R1):



However, measurements often indicate that nighttime concentrations of nitric acid at ground level are below detection limits.

The rate of nitric acid production, via reactions R1 through R5, is a nonlinear function of NO_x concentration. When R1 is limited by OH radical concentrations, decreases in the nonlimiting reactant, NO_2 , will not decrease the rate of HNO_3 formation until NO_2 becomes limiting. Reaction R1 becomes limited by radical concentrations as NO_x concentrations increase, but whether the limiting reactant in reaction R1 is OH radical or NO_2 depends upon the rates of emissions of NO and NO_2 , the rate of conversion of NO to NO_2 , and the rates of production and destruction of OH. Reaction R1 is a sink for OH radical, whereas the competing reaction of OH with hydrocarbon species (RH) regenerates OH radical:



The ratio of hydrocarbon species concentrations to NO_x concentrations is therefore a key determinant of which reactant in R1 limits the rate of production of nitric acid.

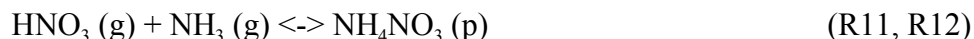
When reaction R1 is NO_2 limited, decreases in NO_x may be expected to decrease the rate

of formation of HNO_3 , and, depending upon other factors, may also decrease the ambient concentrations of particulate nitrate. Conversely, when R1 is radical limited, decreases in VOC may decrease the rate of formation of HNO_3 . However, it is also possible under radical-limited conditions for decreases in VOC to increase HNO_3 levels. This opposing effect may occur when reaction R1 is dominated by the reaction of NO_2 with a radical species derived from either acetaldehyde or acetone to form peroxyacetylnitrate (PAN):



The reverse reaction (R10) has a strong temperature dependence, so that thermal decomposition of PAN can regenerate NO_2 . If VOC reductions shift the fate of NO_2 from PAN production (R9) to HNO_3 formation (R1), increases in particulate nitrate concentrations may occur. However, if R1 is dominant and limited by radical concentrations, further reduction of radical levels through VOC reductions may be expected to decrease HNO_3 formation.

Nitric acid and ammonia (NH_3) establish the following equilibrium:



where “g” and “p” denote the gas and condensed phases, respectively. The formation of particulate nitrate via reaction R11 may be limited by the concentrations of either HNO_3 or NH_3 . Ammonia concentrations, in turn, are affected by concentrations of sulfuric acid (H_2SO_4) and bisulfate (HSO_4^-) via dissociation of aqueous H_2SO_4 and reaction of bisulfate or sulfate with NH_3 :



Ammonia may become limiting in reaction R11 because NH_3 reacts preferentially with H_2SO_4 or HSO_4^- aerosol to form either $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 (R17 and R19). Reductions of SO_2 , while resulting in decreases of aerosol sulfate, can then lead to increases in particulate nitrate, as the ammonia freed by the reverse reactions R18 and R20 becomes available to react with HNO_3 in R11.

Sodium nitrate may also be generated via reaction of nitric acid with sodium chloride in marine aerosol. Whereas ammonium nitrate is typically found in the fine ($PM_{2.5}$) aerosol fraction, sodium nitrate is more likely to occur in the coarse fraction ($PM_{2.5}$ to PM_{10}).

Gas-Particle Equilibrium

Thermodynamic equilibrium models, when applicable, provide a useful description of relations between particulate ammonium nitrate and its gas-phase precursors, ammonia and nitric acid. In addition, equilibrium models can describe the effects of changes in sulfate concentrations on nitrate concentrations. Under some circumstances, though, particulate nitrate and its precursors may be too far from equilibrium for equilibrium models to be even approximately correct. Therefore, the adequacy of the approximation should be checked when applying an equilibrium model.

If thermodynamic equilibrium is an adequate approximation, model simulations show when particulate nitrate will respond to changes in HNO_3 and when it will not. At lower concentrations of ammonia and higher concentrations of HNO_3 or of sulfate, particulate nitrate formation is limited by the available ammonia. Particulate nitrate concentrations then decrease if ammonia concentrations decrease (Figure 3). They increase if sulfate concentrations decrease, and do not change if HNO_3 concentrations decrease (Figure 3).

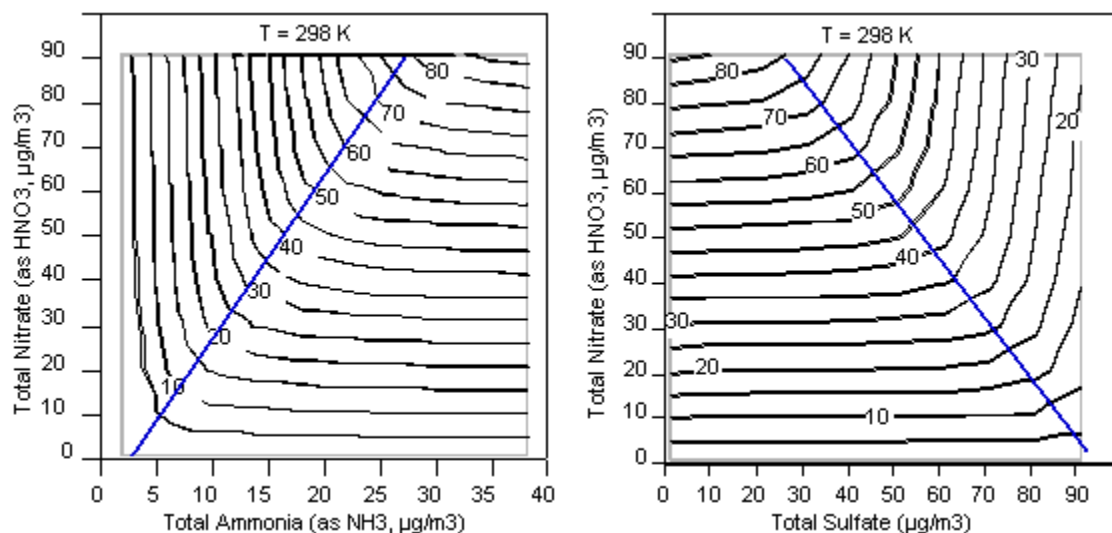


Figure 3. Predicted particulate nitrate concentrations as a function of variations in total nitrate and total ammonia (left panel) or sulfate (right panel). The straight line delineates the points at which total ammonia is equal to total nitrate plus sulfate (molar basis times charge, or equivalents), adjusting for other inorganic species according (see text). It marks a transition between a region where particulate nitrate responds to changes in HNO_3 (below the line) and where it does not (above the line). The region above the line is ammonia limited and has total ammonia concentrations less than the sum of sulfate and total nitrate (equivalents). Source: Blanchard et al. (2000).

The nitrate response that is predicted by thermodynamic equilibrium models has been classified into two or more categories using the values of measurable species. One such parameter is excess ammonia, defined as (Blanchard et al., 2000):

$$\begin{aligned} \text{Excess ammonia} = & [\text{NH}_3 (\text{g})] + [\text{NH}_4^+ (\text{p})] - 2 [\text{SO}_4^{2-} (\text{p})] - [\text{NO}_3^- (\text{p})] - [\text{HNO}_3 (\text{g})] \\ & - [\text{HCl} (\text{g})] + 2 [\text{Ca}^{2+}] + 2 [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] - [\text{Cl}^-] \end{aligned} \quad (1)$$

where all concentrations are in units of $\mu\text{mol m}^{-3}$, and “g” and “p” denote gas and condensed phases, respectively. The set of values for which excess ammonia is zero yields the straight lines demarking the transitions between ammonia and HNO_3 limitation shown in Figure 3. Under many circumstances, principally for measurements of fine particulate, the species shown in the second row of Equation 1 may be neglected because their concentrations are low. The L-shaped contours shown in Figure 3 permit a two-way division of samples into those that are ammonia-limited and those that are HNO_3 limited. However, the contours deviate from the sharp L shapes at higher temperatures and lower relative humidities (e.g., $T > 298\text{K}$ and $\text{RH} < 80$ percent) and at lower temperatures combined with higher relative humidities ($T < 293\text{K}$ and $\text{RH} > 90$ percent). Where the contours are rounded at the transition, or where the isolines deviate more from near-horizontal or near-vertical, the response of particulate nitrate can be more complex and less easily classified into only two categories.

Ansari and Pandis (1998) classify nitrate changes into four general outcomes using the gas ratio, defined as the ratio of free ammonia to total nitrate:

$$\text{Gas ratio} = \text{NH}_3^{\text{F}} / \text{HNO}_3^{\text{T}} \quad (2)$$

$$\text{where } \text{NH}_3^{\text{F}} = [\text{NH}_3 (\text{g})] + [\text{NH}_4^+ (\text{p})] - 2 [\text{SO}_4^{2-} (\text{p})]$$

$$\text{and } \text{HNO}_3^{\text{T}} = [\text{NO}_3^- (\text{p})] + [\text{HNO}_3 (\text{g})] \text{ (molar units)}$$

A gas ratio of one corresponds to excess ammonia of zero (Equation 1, first line only), so that a gas ratio near one (0.4 to 1.5, depending on temperature and RH) delineates a transitional region with nonlinear responses. At higher ratios, ammonia is present in excess and particulate nitrate decreases in response to HNO_3 reductions. At lower ratios (0 to 0.4), ammonia is limiting and particulate nitrate does not decrease in response to HNO_3 reductions, and increases in response to

sulfate decreases. Very low gas ratios (< 0) are acidic samples for which ammonia is so limiting that particulate nitrate concentrations are very low.

Blanchard et al. (2000) characterized ammonia limitation of particulate nitrate formation at California locations using data from the Southern California Air Quality Study (SCAQS), the CADMP, and the 1995 Integrated Monitoring Study (IMS95). Two approaches were used for identifying which reactants (HNO_3 or NH_3) limited the formation of aerosol nitrate. First, a thermodynamic equilibrium model (SCAPE2) was used to predict aerosol nitrate concentrations after either total ammonia or total nitrate concentrations were reduced. These predictions were compared with current particulate nitrate concentrations to determine the fractional nitrate reduction. Calculations were made for mass reductions of either total nitrate or total ammonia of 10, 20, and 40 percent. Second, excess ammonia was computed for each monitoring location using the $\text{PM}_{2.5}$ size fraction measurements of all inorganic species and the measurements of the gas-phase species, nitric acid and ammonia.

The results indicated that the majority of samples had excess ammonia, and that the availability of ammonia did not limit the formation of particulate nitrate at most times and places (Figure 4). The model predicted that the majority of samples having positive excess ammonia would show greater reductions of aerosol nitrate if total nitrate were reduced rather than if total ammonia were reduced (Figure 4). The results for 10 and 40 percent reductions of total nitrate or total ammonia were qualitatively similar to those shown in Figure 4 for 20 percent reductions. In all cases, geographical differences were observed, particularly in the SCAQS data. Many of the ammonia-limited samples were from Burbank; in contrast, most of the ammonia-rich samples were from Riverside.

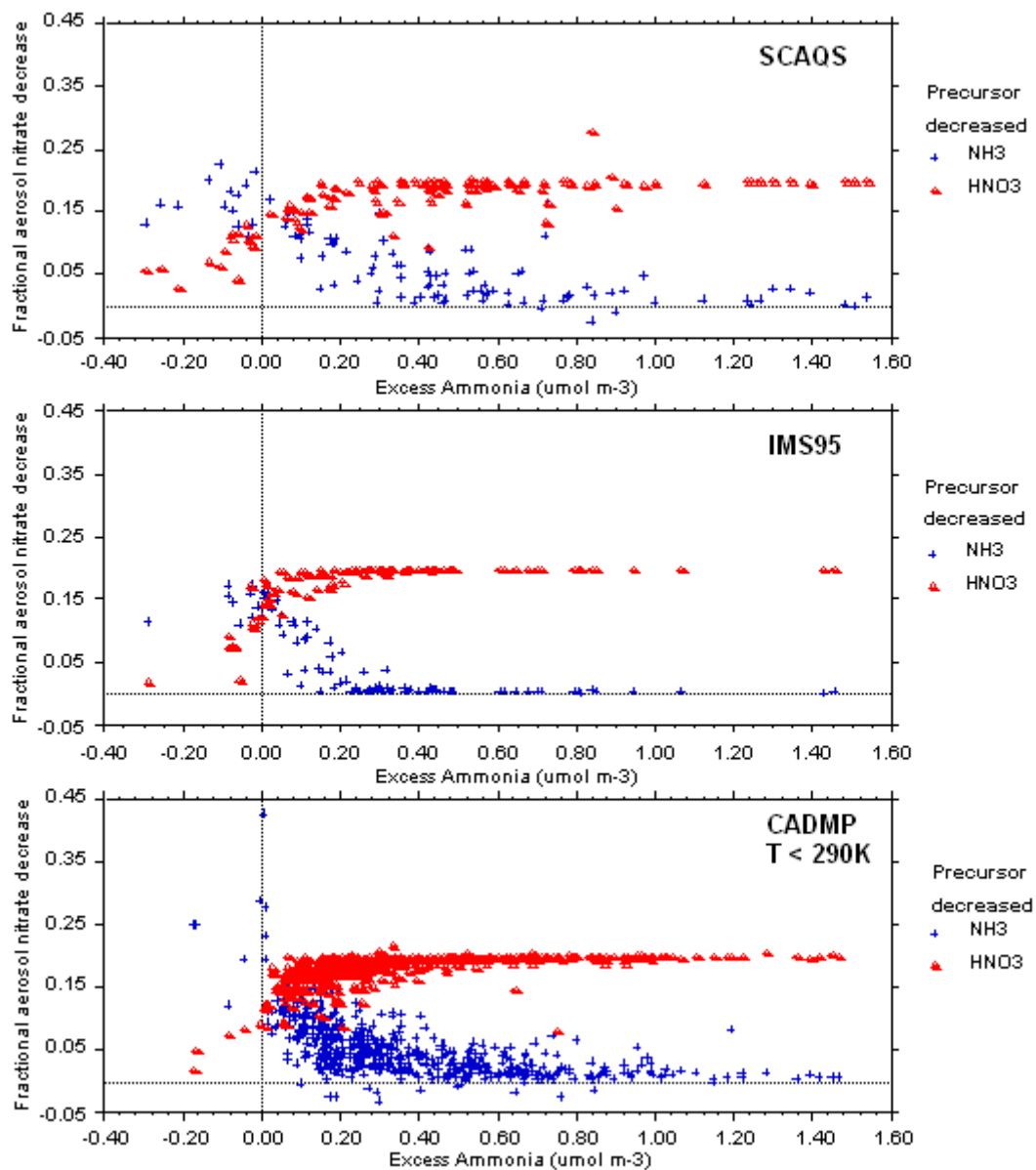


Figure 4. Predicted response of particulate nitrate to reductions of NH_3 or HNO_3 using three data sets (SCAQS, IMS95, and CADMP). The fractional decrease was computed relative to the base case nitrate concentrations. Source: Blanchard et al. (2000).

Blanchard and Tanenbaum (2001; 2003) updated these analyses of which precursor species (ammonia or nitric acid) limit the formation of particulate nitrate in the South Coast Air Basin (SoCAB) using the measurements from the one-year PM₁₀ Enhancement Program (PTEP) study. The data were collected from March 1995 through February 1996 at five locations: Anaheim, downtown Los Angeles, Diamond Bar, Fontana, and Riverside-Rubidoux. Speciated measurements of both PM₁₀ and PM_{2.5} 24-hour samples were made. Gas-phase (ammonia, nitric acid) species were also sampled. SCAPE2 predicted the partition between particulate ammonium and gas-phase ammonia, and between particulate nitrate and gas-phase nitric acid, within about 5 $\mu\text{g m}^{-3}$ for most of the samples. In many cases, the agreement between predicted and measured values was even closer. Given the resolution (24-hour) of the samples, and the temperature- and RH-dependent variations occurring between the gas and particle phases, better agreement between measurements and model predictions may be difficult to achieve. The level of agreement between measurements and predictions was considered adequate for application of the model.

Nearly all PTEP samples showed that particulate nitrate concentrations decreased in response to a 20 percent reduction of total nitrate; in many cases, the predicted decrease was close to twenty percent (Figure 5). In contrast, predicted particulate nitrate concentrations decreased by much smaller amounts in response to a twenty percent decrease in ammonia concentrations and decreases in sulfate concentrations left the particulate nitrate concentrations essentially unchanged. Thus, few samples showed any evidence of ammonia limitation. Emission changes that lower the rates of formation of HNO₃ were therefore predicted to lower particulate nitrate concentrations as well.

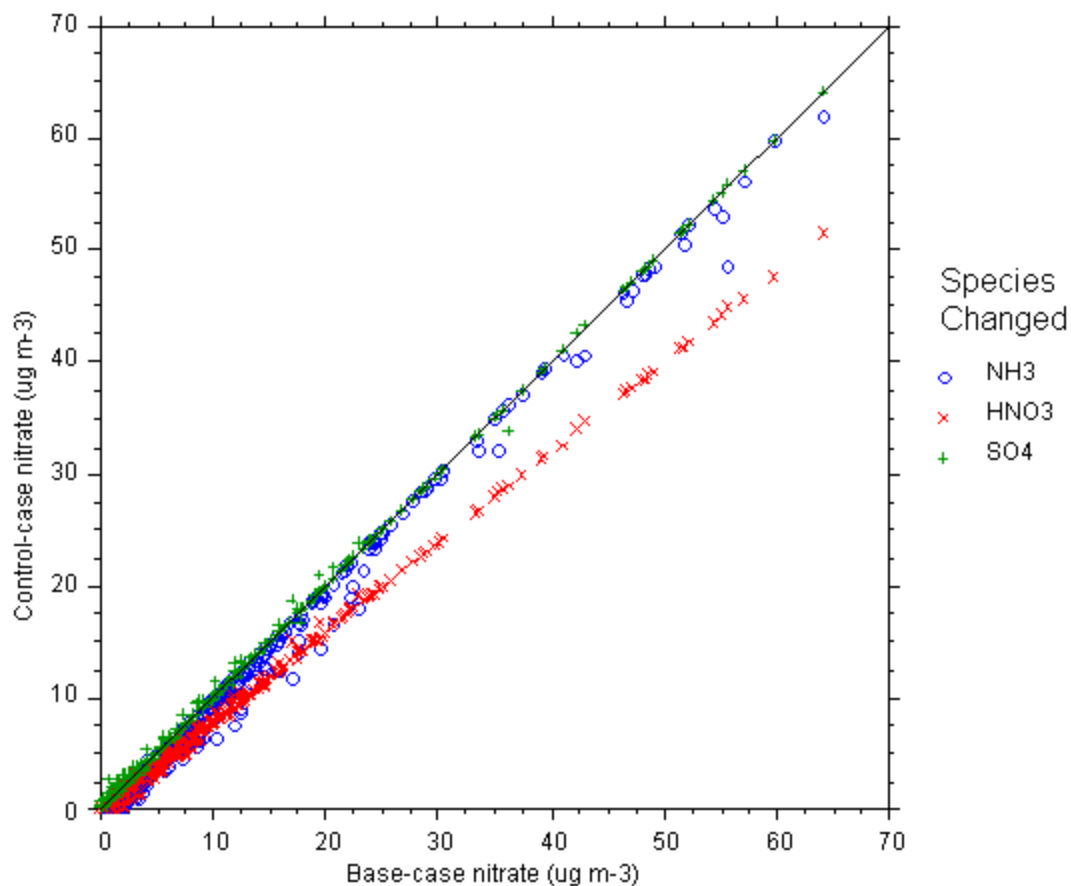


Figure 5. Control-case versus base-case nitrate concentration for 24-hour resolution data from the five sites of the PTEP study. The three control cases (species concentration reductions) were 20 percent decreases of total nitrate (HNO_3 plus particulate nitrate), total ammonia (NH_3 plus particulate ammonium), or sulfate. (Source: Blanchard and Tanenbaum, 2001; 2003).

3. MEASUREMENT ACCURACY

Filter systems are the most commonly employed technique for routinely measuring particle mass and composition. Systems that integrate denuders with filter packs have steadily improved over several decades, reducing interferences and artifacts and thereby improving accuracy, precision, and detection limits (NARSTO, 2002). Accurate determination of particulate nitrate concentrations typically requires the use of denuders, to remove nitric acid, and a back-up filter, to capture nitrate evolving from the dissociation of ammonium nitrate on the primary filter. Systems operated without denuders are subject to positive interference due to the potential capture of nitric acid on the primary filter. Systems operated without a back-up filter are subject to nitrate losses.

Filter systems employing a denuder and a back-up filter provide information on potential nitrate artifacts occurring in systems lacking denuders or back-up filters. With a denuder in place to eliminate or minimize positive artifacts, the nitrate concentrations occurring on the back-up filter indicate the magnitude of nitrate lost from a front filter. Information on positive artifacts can be derived if both denuded and nondenuded channels are operated. Fine-particle nitrate losses and positive artifacts occurring during the one-year PTEP study were estimated by comparing the nitrate levels determined from sequential quartz and nylon filters downstream of a nitric acid denuder with nitrate levels on a quartz filter on a sampler channel lacking a denuder (Kim et al., 1999). Mean annual-average nitrate losses ranged from 1.25 to 2.32 $\mu\text{g m}^{-3}$, in comparison with mean annual particulate nitrate levels of 10.1 to 18.1 $\mu\text{g m}^{-3}$ (Kim et al., 1999). Averaged over the five stations, the mean annual nitrate loss was 1.8 $\mu\text{g m}^{-3}$. On a percentage basis, annual-average nitrate losses varied from 7.3 to 19.8 percent of the mean annual nitrate concentrations. The maximum daily nitrate losses at the stations varied from 6.4 to 22.5 $\mu\text{g m}^{-3}$ (Kim et al., 1999). Nitrate losses were highest during summer and lowest during winter, primarily due to evaporative losses at higher ambient temperatures. However, other loss mechanisms were also identified, including the reaction of ammonium nitrate with strong acids, accounting for the occurrence of high nitrate losses during October as well as during the summer months (Kim et al., 1999). Between 3 and 11 percent of the samples exhibited evidence for the

occurrence of positive artifacts on nondenuded filters, many of which were associated with higher than average concentrations of crustal material. The results were interpreted as indicating chemical reaction of nitric acid with previously collected alkaline soil particles on the quartz filters (Kim et al., 1999).

Hering and Cass (1999) evaluated potential biases in the collection of particulate nitrate by Federal Reference Method (FRM) samplers using data from a 1986 Caltech study and the 1987 Southern California Air Quality Study (SCAQS). The average particulate nitrate concentration from sampling with Teflon filters was 28 percent lower than that determined from denuded nylon filters (Hering and Cass, 1999). Volatilized nitrate concentrations averaged $3 \mu\text{g m}^{-3}$ during October through March and $4 \mu\text{g m}^{-3}$ during April through September, 1986 (Hering and Cass, 1999). Comparison of the SCAQS nitrate concentrations from denuded nylon filters with impactor measurements indicated that positive nitrate artifacts associated with denuded nylon filters were minimal. Clean PM_{10} inlets of the type used in California's dichotomous sampler network have been shown to effectively remove nitric acid (Hering and Cass, 1999).

Evaluations of nitrate artifacts occurring in measurements from California's routine PM_{10} network have not been published. The results of Hering and Cass (1999) and Kim et al (1999) imply, however, that the routine PM_{10} nitrate concentrations are biased by losses of nitrate. Although positive artifacts may occur for some samples, the average annual nitrate losses are probably in the range of 5 to 30 percent of the mean annual nitrate concentrations. These losses affect total mass significantly. Such losses could also obscure observable trends in nitrate levels over time. However, if the PM nitrate measurements are made consistently over a period of time, without change to the measurement system, trends may still be discernable.

A final point of note is that the routine CARB PM_{10} samplers use quartz fiber filters, such as were employed in the PTEP study, rather than Teflon filters, which were studied by Hering and Cass (1999). The slightly lower annual-average loss rates (7 to 20 percent of annual mean nitrate levels) reported by Kim et al (1999) may therefore be more characteristic of the PM_{10} nitrate data than the higher (28 percent) mean loss rate determined by Hering and Cass (1999).

However, nitrate losses depend upon pressure drop within the sampler. Pressure drop in the high-vol ($\sim 1000 \text{ l min}^{-1}$) routine PM_{10} samplers may be substantially different from that occurring in any of the samplers studied by Hering and Cass (1999) and Kim et al (1999).

No evaluations of artifacts associated with the California TSP nitrate measurements have been published. Since the TSP samplers do not employ size-selective inlets of the types used in the PM_{10} dichotomous or SSI samplers, the TSP samplers cannot be assumed to remove nitric acid upstream of the filter. Moreover, the glass fiber filters, especially when they may contain deposited alkaline material, may be expected to adsorb nitric acid. Thus, TSP nitrate measurements may represent total nitrate (nitric acid plus particulate nitrate), rather than particulate nitrate.

4. DATA AVAILABILITY

PM data are available from a variety of long-term routine monitoring programs and short-term special studies in California. As discussed in Section 3, questions exist regarding the accuracy of most of the long-term data; however, the lengthy data records are needed for their statistical power. In contrast, the accuracy of measurements from short-term special studies is typically high, but the shortness of the records can preclude observation of statistically significant trends. Thus, routine data are needed for assessing trends, while special data sets can provide insights into the accuracy and representativeness of routine measurements.

The availability of routine PM data from monitoring networks in California is summarized in Table 1. The networks providing information on particulate nitrate include the TSP, PM₁₀ size-selective inlet (SSI), the California Acid Deposition Monitoring Program (CADMP), the Children's Health Study Two-Week Sampler (CHS TWS), and the IMPROVE networks. Of these networks, ten-year records are available for the TSP, PM₁₀ SSI, IMPROVE, and part of the CADMP networks. The CADMP operated 10 sites from 1988 through 1994 on a once-per-six days, twice-a-day (6 am to 6 pm and 6 pm to 6 am) schedule. In 1995, the network was reduced to three sites in southern California (Long Beach, downtown Los Angeles, and Azusa), plus Fremont and Sacramento. The IMPROVE sites, located in national parks, are of primary interest for characterizing trends in more remote parts of California (Figure 1).

For the present project, data from the TSP and PM₁₀ networks were acquired and analyzed (the five CADMP sites with longer records were also equipped with routine PM₁₀ monitors). This approach maintains a focus on trends in urban and populated areas. Further work would benefit from extending analyses to include IMPROVE or CADMP data. Routine CARB PM₁₀ and TSP samples are collected once every 6 days, for a 24-hour period. The numbers of sites from the South Coast, South Central Coast, and Mojave Desert air basins having data for at least 50 percent of the scheduled sampling days during both cool (October - March) and warm (April - September) seasons are shown in Table 2 for each year.

Table 1. Availability of routine PM data from networks in California (Source: Motallebi et al., 2003a). Not all TSP and SSI sites operated for the entire network operating periods, nor did all sites measure ions (sulfate, nitrate, ammonium, and chloride) in addition to mass.

Network	Operating period	Cutpoints (μm)	Time resolution (hours)	Species measured	Number of sites
TSP	1980 - 1999	none (~30)	24	mass, ions	~70
SSI	1984 - current	10	24	mass, ions	~150
TEOM	1994-current	10	1	mass	35
Dichot	1988 - 1999	10, 2.5	24	mass, elements	20
CADMP	1988 - 1994	10, 2.5	12	mass, ions, elements, gas	10
CADMP	1995 - 1998	10, 2.5	24	mass, ions, elements, gas	5
IMPROVE	1987 - current	10, 2.5	24	mass, ions, elements, gas	8
CHS TWS	1994 - 1999	2.5	2 weeks	mass, ions, acids	12
FRM	1999 - current	2.5	24	mass	73

Table 2. Number of PM sites in the South Coast, South Central Coast, and Mojave Desert air basins having data from fifty percent or more of scheduled sampling days (every sixth day) for both the cool season (October-March) and the warm season (April-September).

Year	PM ₁₀ mass	PM ₁₀ nitrate	PM ₁₀ sulfate	PM ₁₀ ammonium	TSP sulfate	TSP nitrate
1980	0	0	1	0	35	14
1981	0	0	1	0	37	15
1982	0	0	0	0	35	4
1983	0	0	0	0	37	7
1984	0	9	0	0	40	14
1985	9	16	12	0	45	17
1986	12	19	19	0	38	12
1987	27	20	20	8	36	5
1988	36	23	20	7	34	11
1989	44	26	26	7	29	11
1990	45	29	27	7	25	14
1991	45	29	26	6	17	11
1992	51	30	29	6	17	0
1993	54	31	30	5	18	2
1994	50	29	29	4	16	0
1995	47	25	25	6	16	11
1996	52	30	28	6	14	0
1997	49	24	23	6	13	0
1998	45	24	24	6	13	0
1999	44	17	17	0	13	1

Other measurements that were acquired for this project were CO, NMHC, and coefficient of haze (CoH). Coefficient of haze is a measurement of optical attenuation due to absorption by particles, and the principal absorbing species is elemental (black) carbon. Other components of particulate matter may, however, contribute to optical attenuation. CoH measurements are reported in units of 1/1000 feet. The ARB specifies the conversion factor from CoH to light absorption (b_{ap}) as:

$$b_{ap} \text{ (Mm}^{-1}\text{)} = 71 * [\text{CoH (1/1000 ft)}]^{0.76}$$

Light absorption is approximately a linear function of elemental carbon concentration; a proportionality constant (absorption efficiency) of $10 \text{ m}^2 \text{ g}^{-1}$ is sometimes used.

5. PM, NITRATE, AND NO_x TRENDS IN SOUTHERN CALIFORNIA: SUMMARY OF PREVIOUS WORK

In this section, we summarize the nitrate trend analyses from our earlier report, “Analysis of Weekday/Weekend Differences in Ambient Particulate Nitrate Concentrations and Formation in Southern California” (Blanchard and Tanenbaum, 2001; 2003). In that work, trends were studied for each routine monitoring location in the South Coast, South Central Coast, and Mojave Desert air basins having at least 10 years of PM₁₀ or TSP data available for the period 1980-1999. Although restricted to southern California, the sites studied represent approximately two-thirds of the PM nitrate monitoring locations in the state.

Routine PM₁₀ and TSP samples are collected once every 6 days, for a 24-hour period. Twenty-four hour averages (computed from hourly measurements) of NO_x were matched by date to the available PM₁₀ and TSP measurements. The data were split by cool (October - March) and warm seasons (April - September), as well as by weekdays and weekend days. The numbers of sites having at least 50 percent of sampling days during both cool and warm seasons are shown in Table 2 (preceding section) for each year.

The trend analyses summarized in this chapter are less comprehensive than those reported in Sections 6 and 7, and so serve as a starting point for the later work. The analyses of Sections 6 and 7 use monthly concentration averages, whereas those reported here were based upon seasonal averages (e.g., one warm-season, weekday average per year). Also, in Sections 6 and 7 more sophisticated statistical models were developed for seven long-term monitoring sites having measurements of a suite of pollutants. These long-term sites are not restricted to southern California. Here, the trend tests are limited to single-variable linear regression techniques, applied to seasonal pollutant averages at sites in southern California.

In southern California, nitrate levels at some sites were somewhat lower during the period 1995-1999 than during earlier years, although nitrate differences over time were generally less than the magnitudes of the seasonal variations (Figures 6, 7, 8). Note that for splitting the

data into weekdays and weekend days, it was helpful to aggregate the data into five-year periods for these graphical displays (with a sampling frequency of once in six days, it is possible to have no weekend sample days in some months). NO_x levels were significantly lower on weekends than on weekdays, whereas PM_{10} nitrate and TSP nitrate concentrations were not (Blanchard and Tanenbaum 2001; 2003; Figure 6).

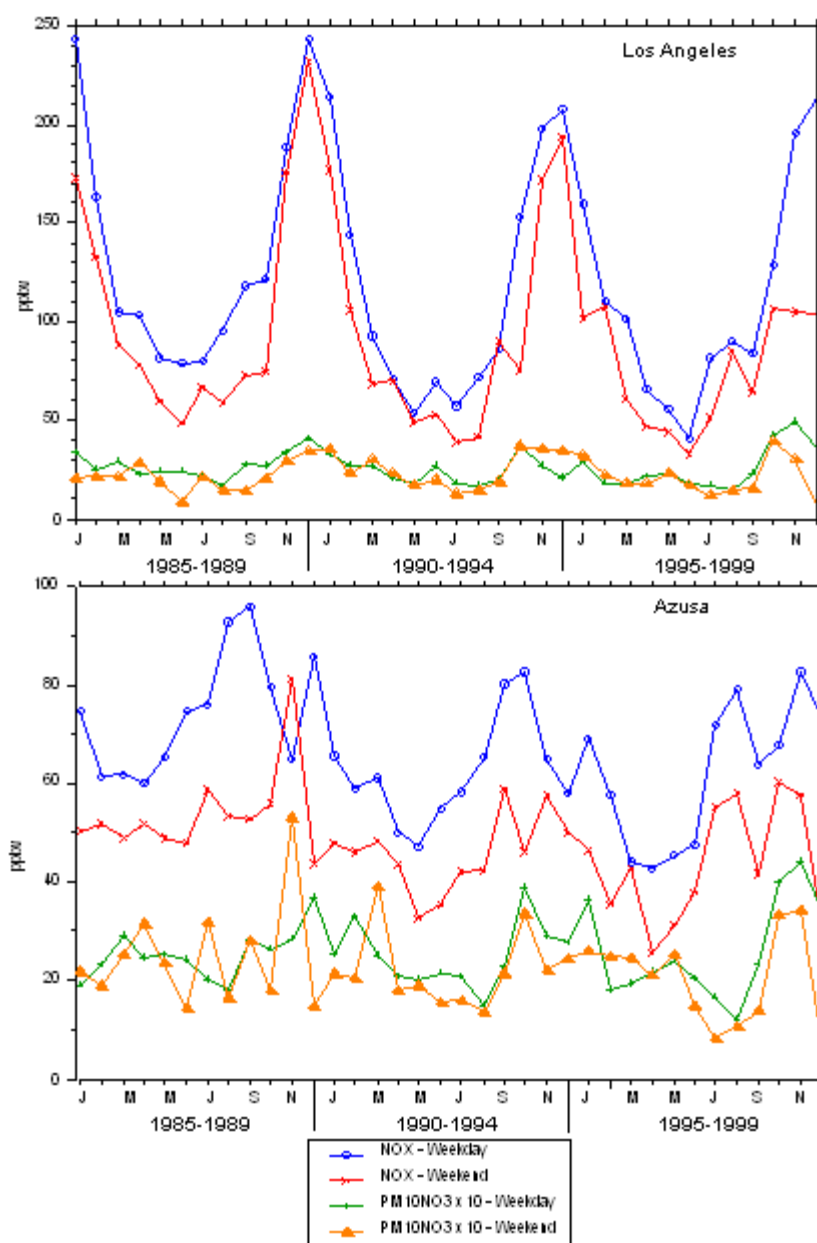


Figure 6. Monthly weekday and weekend averages of NO_x and PM₁₀ nitrate at Los Angeles and Azusa during three time periods. Units of measurement are ppbv, and nitrate concentrations were multiplied by ten.

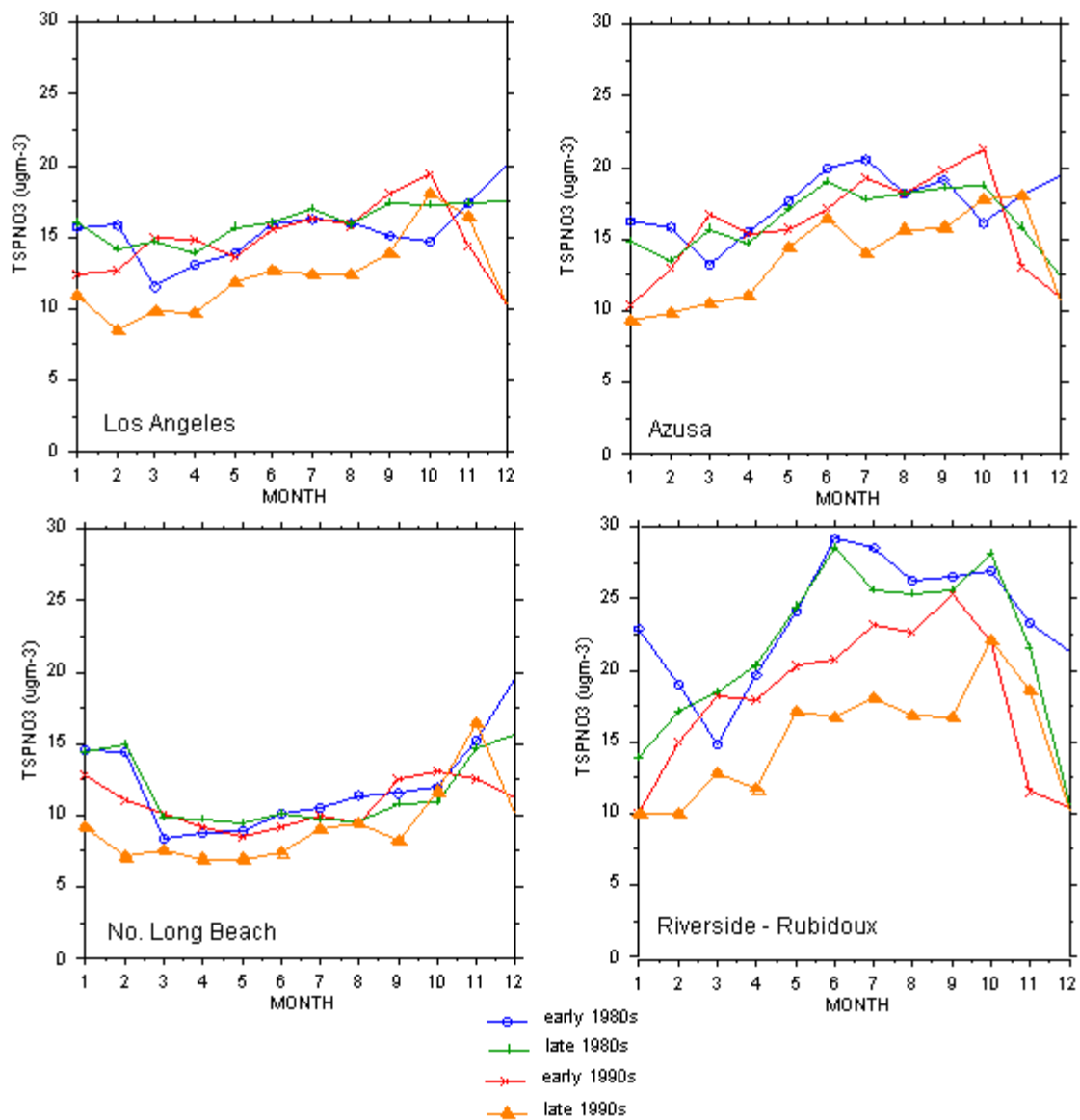


Figure 7. Monthly averages of TSP nitrate, computed from measurements within five-year periods: 1980-1984, 1985-89, 1990-94, and 1995-99.

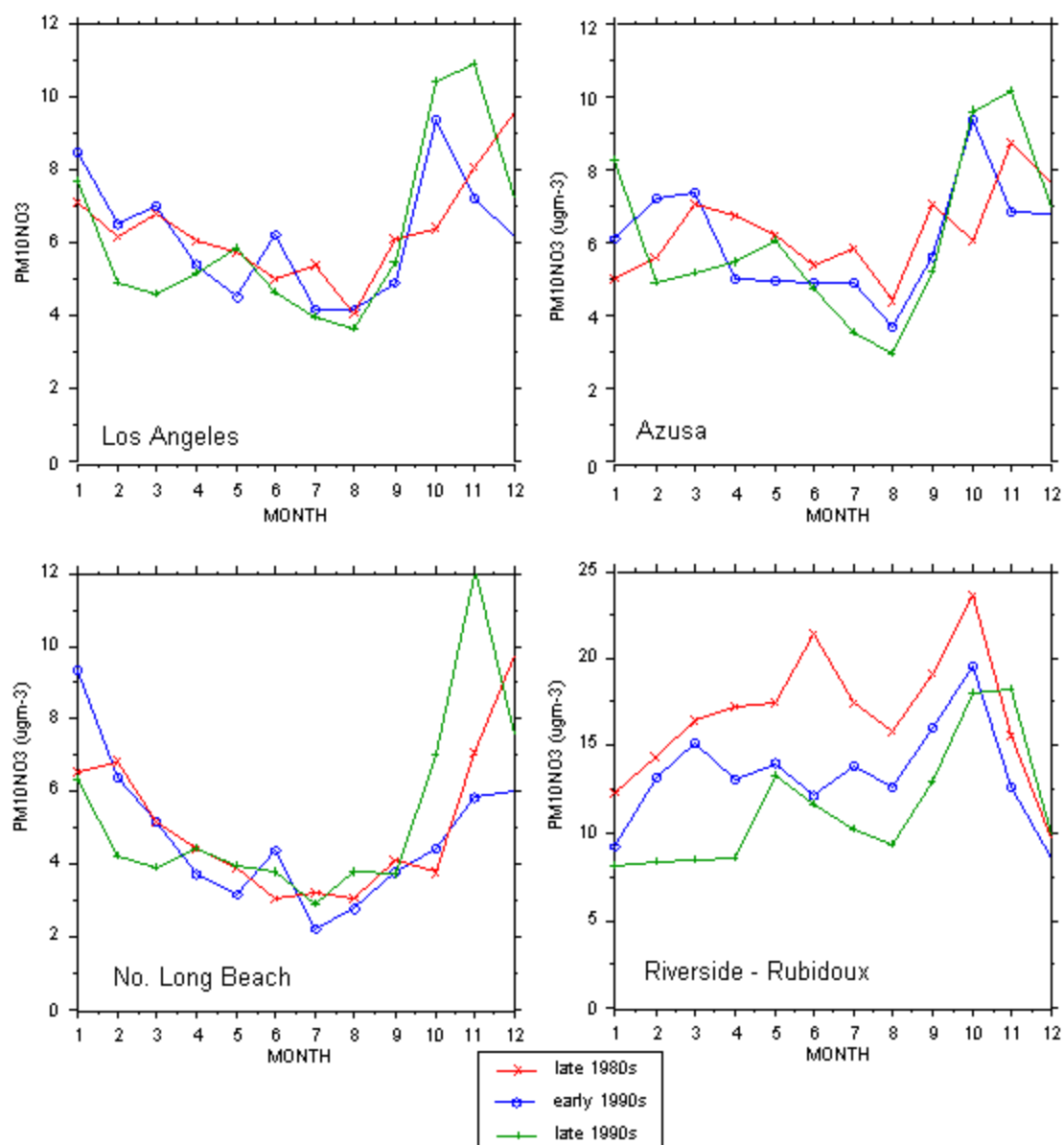


Figure 8. Monthly averages of PM₁₀ nitrate, computed from measurements within five-year periods: 1985-89, 1990-94, and 1995-99. No measurements were made prior to 1985.

Trends were examined systematically using linear regressions of log-transformed mean seasonal concentrations against time (Tables 3 and 4). Specifically, at each site, four averages per year were determined for each species: warm season-weekdays, warm season-weekends, cool season weekdays, and cool season-weekends. The trends for each such series were determined independently by regression against year.

PM₁₀ mass declined at all sites, and TSP mass and NO_x levels declined at most sites; many of these decreases were statistically significant (Table 4). PM₁₀ nitrate and TSP nitrate both declined at most sites, with a few of these declines being statistically significant (Table 4). The average rate of decline of PM₁₀ nitrate was slightly lower during the cool season than the warm season, but this seasonal difference was not statistically significant (Table 3). The average rate of decline of PM₁₀ nitrate exceeded the rate of average rate of decline of NO_x, which suggests that factors in addition to declining NO_x levels influenced the trends in PM₁₀ nitrate. The mean TSP nitrate declines were more similar to the NO_x declines. As discussed in Section 3, TSP nitrate concentrations may include nitric acid as well as particulate nitrate, so that trends in TSP nitrate may differ from trends in PM₁₀ nitrate. Also, the time periods covered by the TSP and PM₁₀ measurements differed, which is another reason that trends in TSP nitrate may differ from trends in PM₁₀ nitrate. The ratios of nitrate to NO_x increased at about half the sites and decreased at about half, with virtually none statistically significant. These contrasts between NO_x and nitrate trends will be examined further in Sections 6 and 7.

Because the data for each site were split into four groups (cool and warm seasons, weekdays and weekends), the inherent noise in the data limits the ability to detect trends, as indicated by the average trends and standard errors (Table 3). Thus, for some species, including PM₁₀ nitrate and TSP nitrate, few results were statistically significant (Table 4). The trend analyses discussed in Sections 6 and 7 use different statistical methods that do not require splitting the data into separate subsets.

Table 3. Average slope and standard error for regressions of annual-average PM₁₀, TSP, PM₁₀ NO₃, TSP NO₃, NO_x, PM₁₀ NO₃/NO_x, and TSP NO₃/NO_x against year, split by warm (April-Sept) or cool (October-March) seasons and day of week (weekend or weekday). Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 10 or more years of data from 1980 through 1999.

Species	Season	Days	No. Of Sites	Mean Slope (% year ⁻¹)	Mean SE of Slope (%/yr)
PM ₁₀	warm	weekday	9	-3.33	0.83
	warm	weekend	9	-3.33	0.90
	cool	weekday	9	-3.47	1.02
	cool	weekend	9	-3.99	1.47
TSP	warm	weekday	27	-1.87	0.78
	warm	weekend	27	-1.84	0.93
	cool	weekday	27	-1.33	1.12
	cool	weekend	27	-2.74	1.64
PM ₁₀ NO ₃	warm	weekday	9	-2.22	1.75
	warm	weekend	9	-2.44	2.01
	cool	weekday	9	-1.70	1.94
	cool	weekend	9	-1.61	2.86
TSP NO ₃	warm	weekday	21	-1.28	0.77
	warm	weekend	21	-1.66	1.06
	cool	weekday	21	-1.28	1.25
	cool	weekend	21	-1.37	1.87
NO _x	warm	weekday	20	-1.18	1.11
	warm	weekend	19	-1.78	1.32
	cool	weekday	20	-0.38	0.88
	cool	weekend	20	-1.34	1.51
PM ₁₀ NO ₃ /NO _x	warm	weekday	9	0.15	1.82
	warm	weekend	9	-0.31	2.28
	cool	weekday	9	-0.39	2.06
	cool	weekend	9	0.84	2.51
TSP NO ₃ /NO _x	warm	weekday	16	-0.44	1.16
	warm	weekend	16	0.06	1.51
	cool	weekday	16	-1.49	1.29
	cool	weekend	16	-0.56	1.52

Table 4. Number of sites in the South Coast, South Central Coast and Mojave Desert Air Basins that have statistically significant ($p < 0.01$) decreasing or increasing trends of annual-average PM_{10} , TSP, $PM_{10} NO_3$, TSP NO_3 , NO_x , $PM_{10} NO_3/NO_x$, and TSP NO_3/NO_x concentrations by warm (April - September) or cool (October - March) season and period (weekday or weekend). Sites were included if they had 10 or more years of data from 1980 through 1999.

Species	Season	Period	Decreasing trends		Increasing trends	
			No. Sites	No. Sig.	No. Sites	No. Sig.
PM_{10}	warm	week day	9	7	0	0
	warm	weekend	9	7	0	0
	cool	week day	9	3	0	0
	cool	weekend	9	3	0	0
TSP	warm	week day	23	16	4	0
	warm	weekend	25	12	2	0
	cool	week day	22	9	5	0
	cool	weekend	24	10	3	0
$PM_{10} NO_3$	warm	week day	7	1	2	0
	warm	weekend	7	2	2	0
	cool	week day	7	0	2	0
	cool	weekend	6	1	3	0
TSP NO_3	warm	week day	19	3	2	0
	warm	weekend	20	3	1	0
	cool	week day	17	6	4	0
	cool	weekend	17	2	4	0
NO_x	warm	week day	15	10	5	0
	warm	weekend	17	9	2	0
	cool	week day	15	5	5	2
	cool	weekend	15	4	5	0
$PM_{10} NO_3/NO_x$	warm	week day	5	0	4	1
	warm	weekend	6	0	3	1
	cool	week day	4	1	5	0
	cool	weekend	2	0	7	0
TSP NO_3/NO_x	warm	week day	7	0	9	1
	warm	weekend	6	0	10	1
	cool	week day	13	3	3	0
	cool	weekend	10	1	6	0

Day-of-week variations occur in PM₁₀ mass, PM₁₀ nitrate and PM₁₀ sulfate concentrations (Blanchard and Tanenbaum, 2001; 2003), as shown for Azusa and Riverside-Rubidoux over the time period 1985 through 1999 (see Figures 9 and 10). PM₁₀ mass shows lower weekend values, whereas PM₁₀ nitrate and PM₁₀ sulfate exhibit neither lower nor higher weekend values. These figures also show declining levels of PM₁₀ mass over time at both Azusa and Riverside. In addition, Figures 9 and 10 reveal decreasing trends for PM₁₀ nitrate measurements at Riverside, but suggest that nitrate concentrations at Azusa may have increased during the cool season while decreasing during the warm season. This result was borne out by the regressions, but appears unique to Azusa. As previously noted, the average PM₁₀ nitrate trends across all sites were not significantly different between warm and cool seasons (Table 4). For Azusa, PM₁₀ nitrate concentrations declined by 1.5 percent (weekdays) and 2.9 percent (weekends) per year during the warm season; during the cool season, they declined by 0.1 percent per year (weekdays) and increased by 1.3 percent per year (weekends). None of these PM₁₀ nitrate trends at Azusa were statistically significant, however.

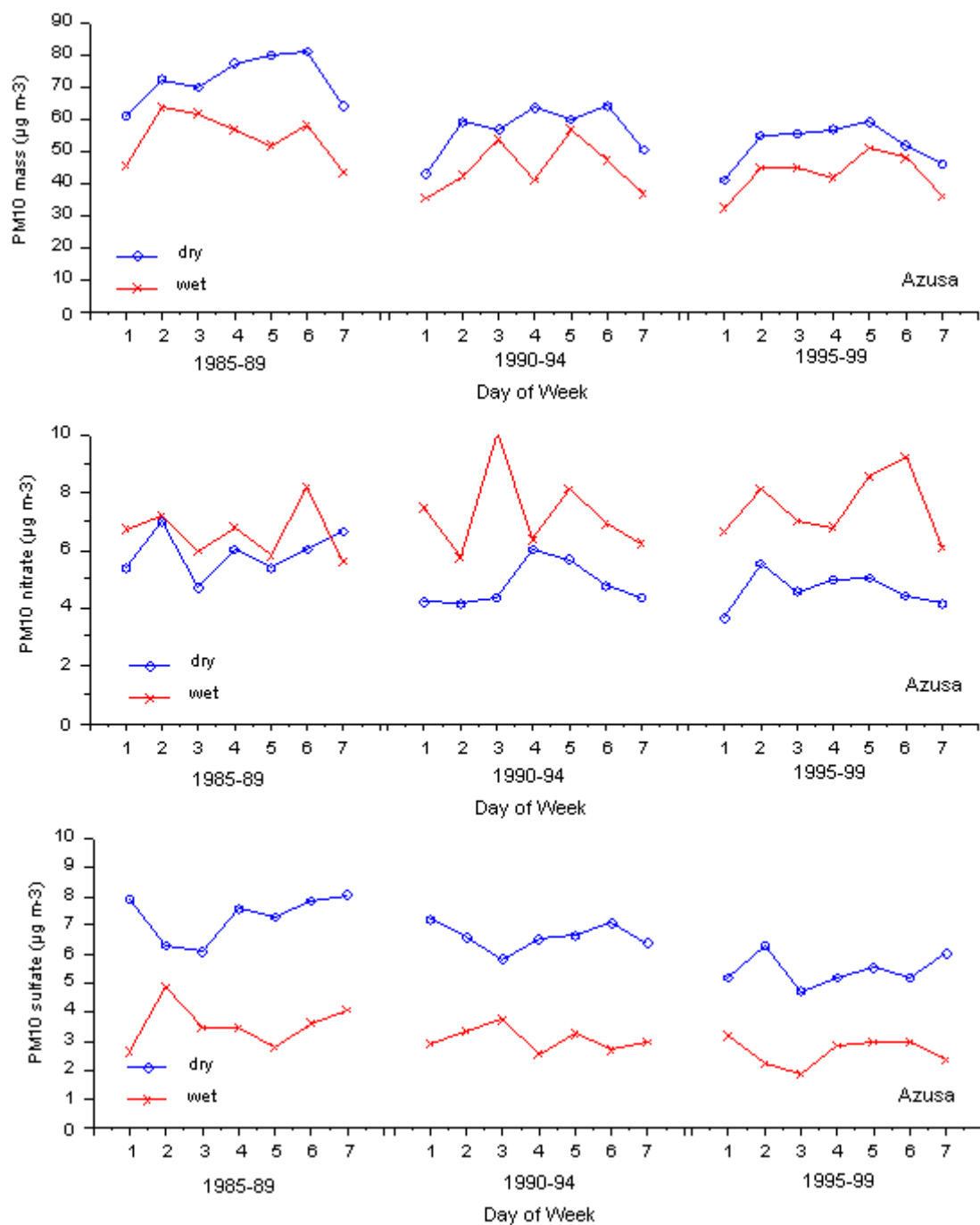


Figure 9. Day of week variations of PM₁₀ mass, PM₁₀ nitrate concentration, and PM₁₀ sulfate by season at Azusa. The seasons are cool (wet) from October through March and warm (dry) from April through September. The samples were collected once every six days from 1985 through 1999. Each point is the average of 60 to 66 samples. Day 1 is Sunday.

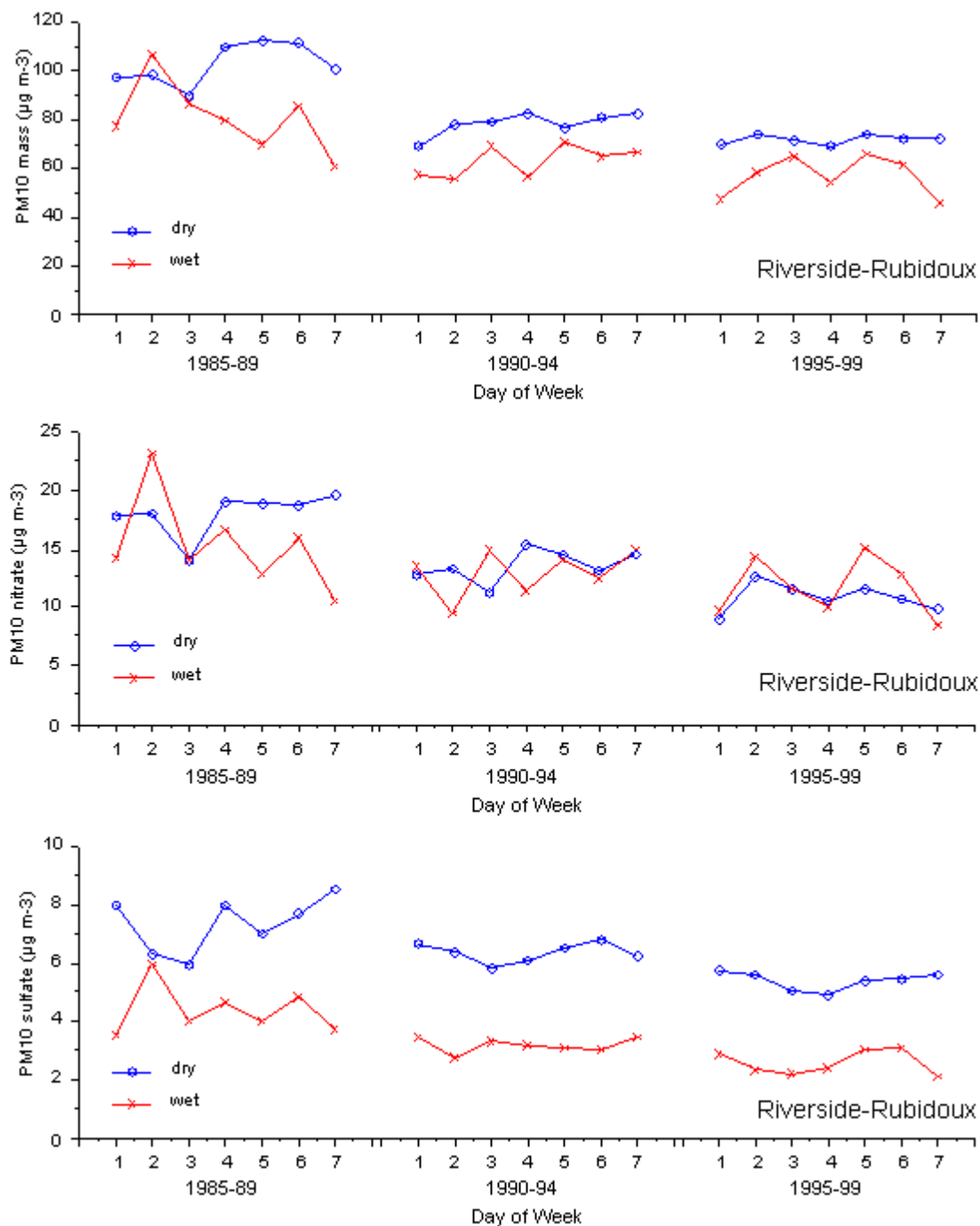


Figure 10. Day of week variations of PM₁₀ mass, PM₁₀ nitrate concentration, and PM₁₀ sulfate by season at Riverside. The seasons are cool (wet) from October through March and warm (dry) from April through September. The samples were collected once every six days from 1985 through 1999. Each point is the average of 60 to 66 samples. Day 1 is Sunday.

6. METHODS FOR NEW TREND ANALYSES

Overview

To evaluate the causal connection, if any, between NO_x and particulate nitrate levels at monitoring locations in California, trends in NO_x , PM_{10} mass, PM_{10} nitrate, TSP mass, and TSP nitrate were quantified and compared statistically. No single method for detecting trends in precipitation chemistry and deposition is considered optimal, or even appropriate, for all purposes (Holland and Sirois, 2001). Two types of statistical analyses were carried out for this project. First, to expand upon the previously-completed trend analyses for sites in southern California, trends in NO_x , PM_{10} mass, PM_{10} nitrate, TSP mass, and TSP nitrate were re-analyzed for each monitoring location in the South Coast, South Central Coast, and Mojave Desert air basins using simple linear regression. Since the time resolution and frequency of sampling varied among compounds, measurements were recompiled as monthly averages prior to analyzing for trends. The monthly averages were seasonally adjusted, as discussed further below, and the trends in these adjusted monthly average concentrations were evaluated for each location having data for at least 60 months using simple linear regression. The data series consisting of seasonally-adjusted monthly averages have more data points (degrees of freedom) than the seasonal and weekday/weekend average yearly concentrations that were analyzed in the earlier work (Section 5), and the results from the new regressions are discussed further in Section 7.

A second set of trend analyses was carried out for a limited number of monitoring sites using both simple linear and stepwise multiple regression to more explicitly examine the relations between particulate nitrate, precursor species, and physical factors. Trend statistics were compiled for long-term (10 years or more) monitoring sites in the South Coast, San Joaquin Valley, and San Francisco Bay Area air basins for the period 1980-2000. In addition, trends in precipitation, ambient CO, coefficient of haze (CoH), and nonmethane hydrocarbons (NMHC) were evaluated at long-term monitors. Again, since the time resolution and frequency of sampling varied among compounds, measurements were recompiled as monthly averages prior to analyzing for trends.

Site Selection

Since the focus of this work was on PM nitrate, the species of particular interest are NO_x , TSP mass, PM_{10} mass, TSP nitrate, and PM_{10} nitrate. For assessing the individual species trends in southern California, all monitoring locations with data for at least ten years for any of these species were included. For the stepwise multiple regression trend analyses, sites in the San Francisco Bay Area Air Basin, San Joaquin Valley Air Basin, and the South Coast Air Basin were reviewed to select monitors that had a minimum of ten years of data during the period 1980-2000 for each of the five species. Sites that met this criterion were Azusa, Riverside, San Bernardino, Visalia, Livermore, Fremont, and Napa. While trends in temperature, precipitation, ambient CO, coefficient of haze (CoH), and nonmethane hydrocarbons (NMHC) were also evaluated at these long-term monitors, we did not require that each of these latter measurements be available because doing so would have eliminated nearly all monitoring locations from consideration.

Averaging Procedures

The data were converted to standardized monthly and 6-month averages to facilitate statistical analysis over time. Data were tested for a minimum of 75 percent completeness within each averaging period; averages not meeting this criterion were identified. NO_x , measured hourly each day, was first averaged requiring a minimum of 18 hours of measurements each day. Monthly NO_x averages with fewer than 21 days for each month were marked. Measurements of CO, CoH, and ozone were treated similarly to NO_x (CoH is measured with two-hour resolution). TSP, PM_{10} , TSP nitrate and PM_{10} nitrate are measured over a 24-hour period on a once-every-six days schedule; monthly averages with fewer than 3 days were identified. Any exclusions of data not meeting these completeness criteria are specifically noted.

For most sites and compounds, the distributions of the monthly averages were not significantly different from lognormal, so all monthly concentration averages were transformed by taking natural logarithms. The time series of monthly-average species concentrations

exhibited long-term trends (not necessarily linear), with larger short-term (monthly or seasonal) variations superimposed.

Simple Linear Regression Using Seasonally-Adjusted Monthly Concentrations

As previously noted, the seasonal variations in PM mass and other pollutants greatly exceed the time trends (Section 5, Figures 6, 7, 8). Analyses using monthly data may therefore benefit from either modeling or removing the seasonal variation. For the simple linear regressions, the seasonal variation was removed as follows:

$$\text{Adjusted } C_{ij} = C_{ij} / C_{\cdot j}$$

where C_{ij} is the average for year i and month j and $C_{\cdot j}$ is the mean month j concentration for all years (e.g., the mean of all January monthly averages). Thus, for each month j , monthly averages exceeding the mean of all such months (e.g., January) have adjusted C_{ij} greater than one. The seasonally adjusted monthly averages were assumed to be uncorrelated, which is a reasonable approximation for sampling frequencies of once in six days. Examples of simple linear regression using seasonally adjusted monthly concentrations are shown in Figure 11. Note that linear regressions were also carried out without seasonal adjustment of the monthly averages. Seasonal adjustment did not change the regression slopes, but did remove the seasonal variations and thereby made the long-term trends more evident.

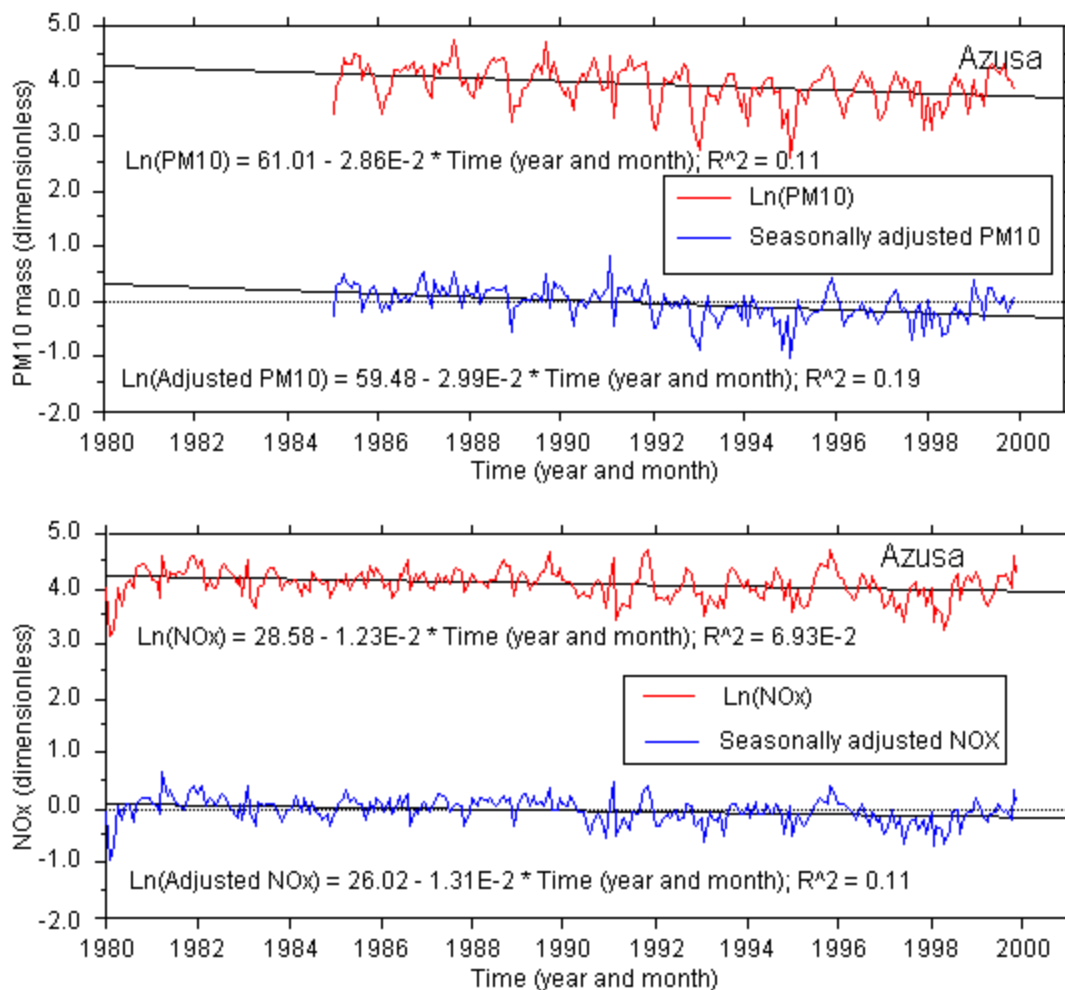


Figure 11. Examples of simple linear regressions for unadjusted and seasonally adjusted monthly average PM_{10} mass and NO_x concentrations at Azusa. Since the averages were transformed by taking logarithms, the regression slopes, when multiplied by 100, give linear trends in units of percent per year. Seasonal adjustment did not significantly change the regression slopes, but did remove the seasonal variations and make the long-term trends more evident.

Stepwise Multiple Regression Applied to Long-Term Monitoring Locations

For the seven long-term monitoring sites, three approaches were used to characterize long-term concentration variations (trends). First, a three-year moving average was determined for each compound at each site. The moving averages remove the seasonal fluctuations, as well as some short-term (e.g., annual) variability. The moving averages were examined graphically.

Second, seasonal variations were explicitly included in a statistical model, which was developed using stepwise multiple regression as described below. Finally, for comparison, we also computed warm and cool season averages. Six-month averages were computed for each year: January - March combined with October - December for the cool season; April - September for the warm season. This combination of months was selected to provide six months per average without losing cool-season averages for the first and last years.

The independent variables used in the stepwise multiple regressions were monthly precipitation amount, temperature, and time for all species; in addition, NO_x, CO, and CoH were included as independent (predictor) variables for PM₁₀ nitrate and TSP nitrate. Sine and cosine terms, which varied by month, were included to represent seasonal variations that were not already represented by temperature and precipitation (if any). For determining time trends, both linear and cyclical components were tested (Sirois, 1999). This procedure allows for the possibility of nonlinear trends. Cyclical components having periods of four, five, and six years were entered into the regressions and retained if statistically significant. As an example, the full regression equation for PM₁₀ nitrate was:

$$\begin{aligned}\ln(\text{PM}_{10} \text{ nitrate}) = & a_0 + a_1(\text{precipitation}) + a_2 \ln(\text{NO}_x) + a_3 I_{\text{cool}} \ln(\text{NO}_x) \\ & + a_4 \text{time} + a_5 I_{\text{cool}} \text{time} + a_6(\text{temperature}) \\ & + b_1 \sin((2\pi \text{time} - 1980)/4) + b_2 \cos((2\pi \text{time} - 1980)/4) \\ & + b_3 \sin((2\pi \text{time} - 1980)/5) + b_4 \cos((2\pi \text{time} - 1980)/5) \\ & + b_5 \sin((2\pi \text{time} - 1980)/6) + b_6 \cos((2\pi \text{time} - 1980)/6) \\ & + c_1 \sin((2\pi \text{month} - 1)/12) + c_2 \cos((2\pi \text{month} - 1)/12) \\ & + d_1 \ln(\text{CO}) + d_2 \ln(\text{CoH})\end{aligned}$$

where:

time = calendar year + (month-1)/12

$I_{cool} = 1$ for January, February, March, October, November, and December

$= 0$ for March - September

and $\ln(\text{PM}_{10} \text{ nitrate})$, $\ln(\text{NO}_x)$, $\ln(\text{CO})$, and $\ln(\text{CoH})$ are monthly averages

The cool-season indicator, I_{cool} , was used to differentiate warm-season and cool-season trends or relations to NO_x . Not all components were statistically significant for all regressions.

For the regressions involving monthly average $\ln(\text{PM}_{10} \text{ nitrate})$ or $\ln(\text{TSP nitrate})$, $\ln(\text{NO}_x)$, $\ln(\text{CO})$, and $\ln(\text{CoH})$ were included to permit examination of the hypothesis that trends in primary pollutant concentrations have affected trends in nitrate. Some of the difficulties in establishing linkages between primary pollutant trends and secondary pollutant trends include measurement inaccuracies and sampling frequency (Section 3) and inferring causality from correlation (Section 7). Besides the measurement issues associated with nitrate (Section 3), biases and uncertainties exist also in measurements of NO_x and CoH, which are not discussed here. For the purposes of this study, NO_x measurements, which are known to include reaction products such as peroxyacetylnitrate (PAN) and nitric acid in addition to NO and NO_2 , are used as the only available long-term surrogate for NO_y .

The regressions were not intended to evaluate the consistency of trends in the ambient concentrations of CO, NO_x , and PM_{10} mass with emission inventory estimates. Obvious discrepancies have been noted, however.

7. RESULTS OF NEW TREND ANALYSES

Simple Linear Regressions for Sites in Southern California

The results of the simple linear regressions of seasonally-adjusted monthly concentrations for sites in southern California are summarized in Table 5. Decreasing trends were evident for all compounds at the majority of monitoring sites: PM₁₀ mass (50 of 53 sites declined, with 37 declines statistically significant), NO_x (34 of 48 sites declined, with 25 declines statistically significant), PM₁₀ nitrate (20 of 25 sites declined, with 12 declines statistically significant), and TSP nitrate (25 of 38 sites declined, with 13 declines statistically significant). A greater fraction of sites showed declining (and significantly declining) trends in PM₁₀ mass and PM₁₀ nitrate than in NO_x, and the mean declines in PM₁₀ mass and PM₁₀ nitrate exceeded the mean decline in NO_x (Table 5).

Table 5. Summary of simple linear regression trend analyses for sites in southern California. The number of statistically significant ($p < 0.01$) results is indicated. All sites had measurements from at least 60 months within the period from 1980 through 1999.

Species	Number sites decreasing	Number sites decreasing and significant	Number of sites increasing	Number of sites increasing and significant	Mean trend, % per month (Mean S.E.)
PM ₁₀ Mass	50	37	3	0	-0.246 (+/- 0.071)
NO _x	34	25	14	5	-0.080 (+/-0.080)
PM ₁₀ NO ₃	20	12	5	0	-0.304 (+/-0.109)
TSP NO ₃	25	13	13	1	-0.044 (+/-0.100)
PM ₁₀ NO ₃ / NO _x	9	5	6	2	-0.153 (+/-0.107)
TSP NO ₃ / NO _x	9	4	13	2	0.035 (+/-0.083)

Trends in TSP nitrate were less pronounced than were trends in PM₁₀ nitrate (Table 5). As discussed in Section 3, TSP nitrate concentrations may include nitric acid as well as particulate nitrate, so that trends in TSP nitrate may differ from trends in PM₁₀ nitrate. Also, the time periods covered by the TSP and PM₁₀ measurements differed (approximately 1980-95 for TSP nitrate and 1985-99 for PM₁₀ nitrate), so that downward trends in TSP nitrate could be less pronounced than downward trends in PM₁₀ nitrate if the rate of nitrate decreases accelerated over time (the data are insufficient to distinguish between linear and nonlinear trends).

Further analysis of these trend results indicates that no geographical consistency occurred in the declining trends for NO_x and PM₁₀ nitrate (Figure 12). The NO_x declines tended to be greater near the coast, whereas the PM₁₀ nitrate declines tended to be greater in the more northern areas. Of 16 sites with both NO_x and PM₁₀ measurements, five showed opposite trends in NO_x and PM₁₀ nitrate concentrations (2 had increasing PM₁₀ nitrate with decreasing NO_x, while three had decreasing PM₁₀ nitrate with increasing NO_x) (Figure 13). Six sites showed trends in PM₁₀ nitrate and NO_x that were directionally the same but differed in magnitude by factors of two to four. Five sites (Anaheim, Azusa, Burbank, San Bernardino, and Santa Clarita) showed quantitatively similar trends for NO_x and PM₁₀ nitrate.

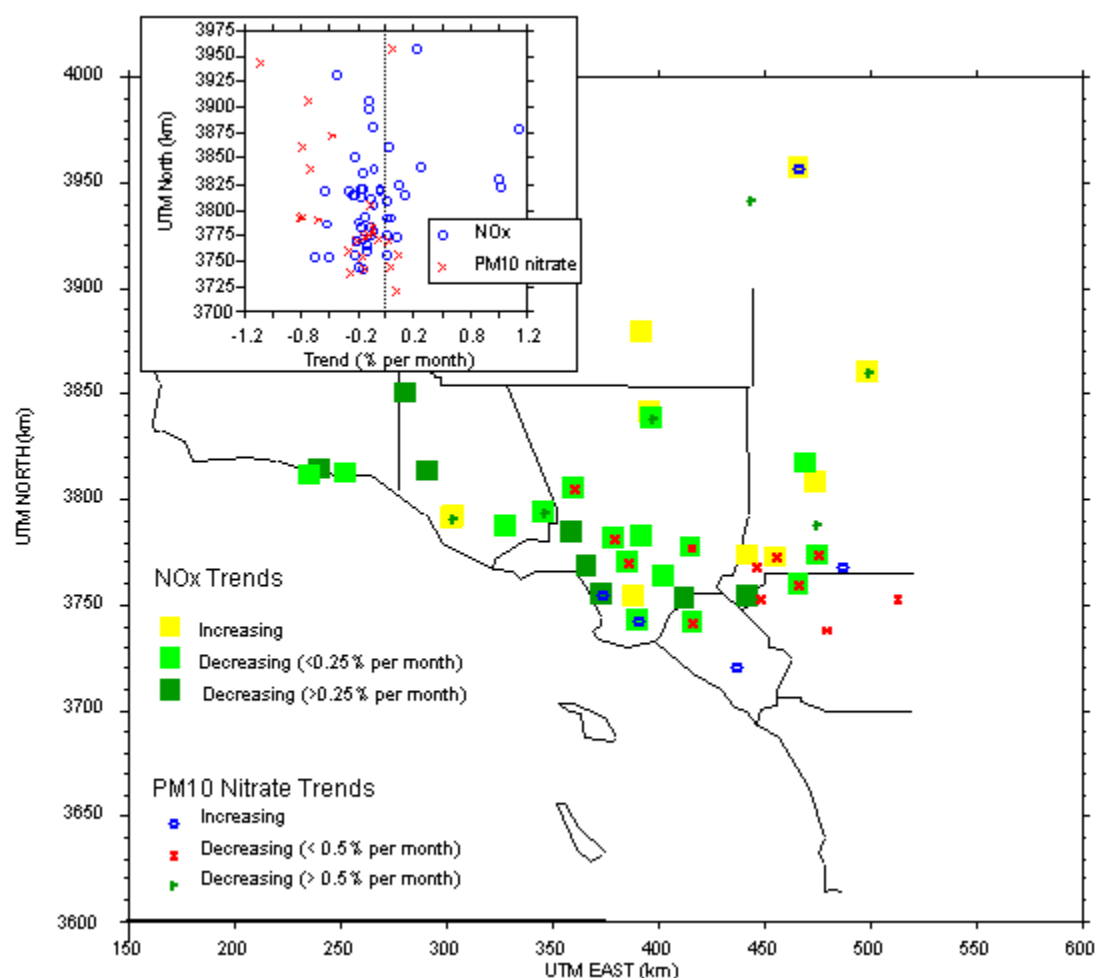


Figure 12. Comparison of NO_x and PM_{10} nitrate trends at sites in southern California. Tests were applied to each compound at each location having at least 60 months data from 1980 through 1999. The trend tests were simple linear regressions of log-transformed seasonally adjusted monthly average concentrations against time, as described in the text. The inset shows trend results plotted against the sites' UTM North coordinates. No geographical consistency between NO_x trends and PM_{10} nitrate trends is evident in either the map or the inset.

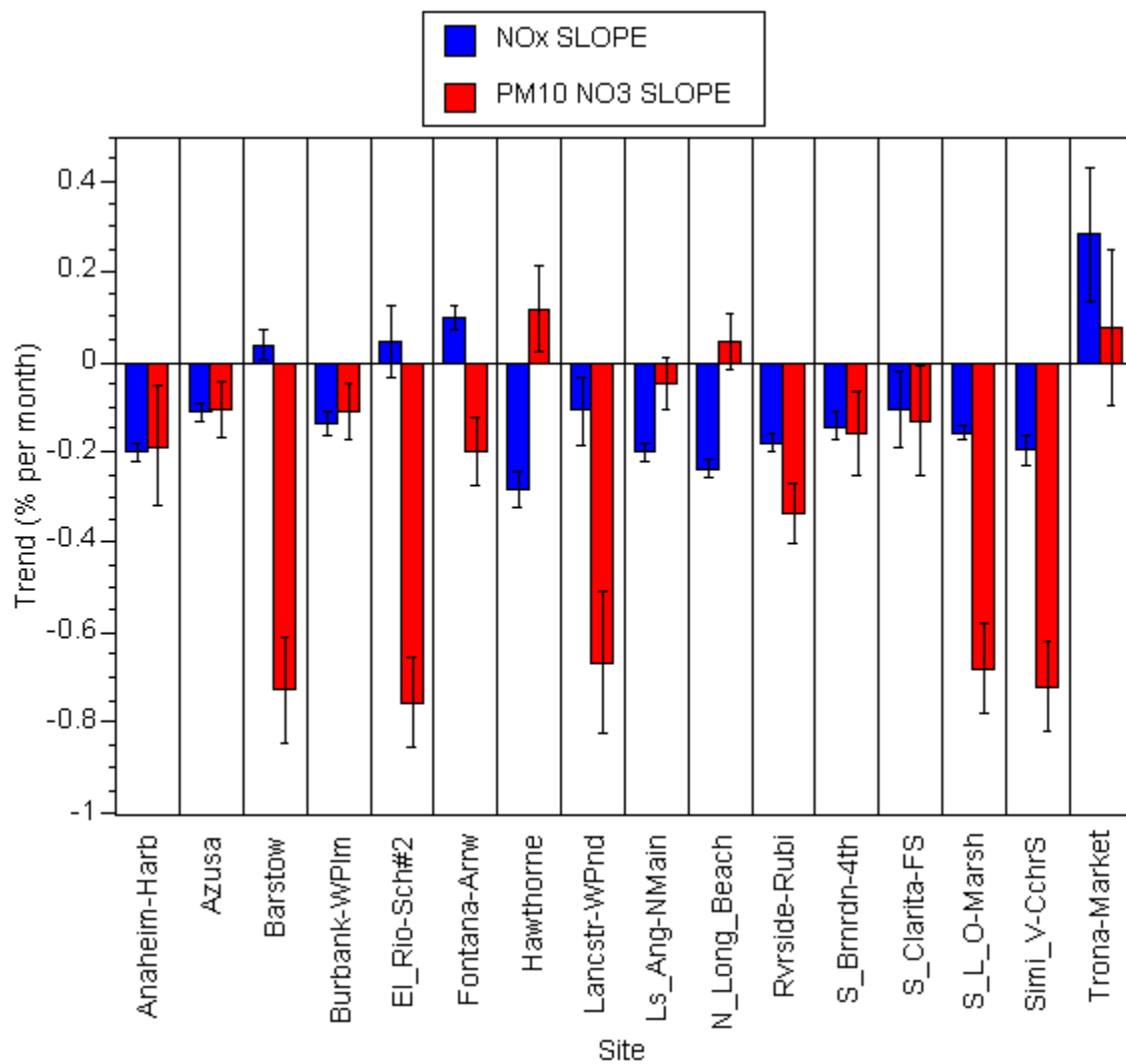


Figure 13. Comparison of trends in monthly-average NO_x and PM_{10} nitrate at sites in southern California. The error bars are one standard error of the regression slope. Trend tests were applied to each location having at least 60 months data from 1980 through 1999.

Simple Linear Regressions for Long-term Monitoring Sites

Simple linear regressions were carried out for each of the seven long-term monitoring sites for PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, NO_x, ozone, CoH, and CO. These regressions describe the simple linear trends in each pollutant at each monitoring location. The monthly average concentrations were not seasonally adjusted prior to testing for trends, because, as shown above, linear regression slopes were not changed by seasonal adjustment. Also, for these long-term sites, statistical models were subsequently developed that explicitly incorporated terms to describe seasonal variability. The results of applying simple linear regressions to the data from the seven long-term monitoring sites are summarized in Table 6. Figure 14 provides an example of the monthly time series of each pollutant at San Bernardino. As was the case for the majority of monitoring sites in southern California, the rates of decline of PM₁₀ nitrate at six of these seven long-term monitoring sites exceeded the rates of decline of NO_x (Table 6 and Figure 15). Only at Azusa is the rate of decline of PM₁₀ nitrate less than the decline of NO_x. The closest matches to the trends in PM₁₀ nitrate concentrations are the trends in CoH (black carbon) and in PM₁₀ mass.

At most sites, trends in TSP nitrate were less pronounced than were trends in PM₁₀ nitrate (Table 6). As discussed in Section 3, TSP nitrate concentrations may include nitric acid as well as particulate nitrate, so that trends in TSP nitrate may differ from trends in PM₁₀ nitrate. Also, the time periods covered by the TSP and PM₁₀ measurements differed (approximately 1980-95 for TSP nitrate and 1985-99 for PM₁₀ nitrate), so that downward trends in TSP nitrate could be less pronounced than downward trends in PM₁₀ nitrate if the rate of nitrate decreases accelerated over time (the data are insufficient to distinguish between linear and nonlinear trends).

Table 6. Summary of linear regression trends in monthly-average concentrations at seven long-term monitoring sites. Trends are expressed as percent per year, with standard errors indicated in the second row for each site. Statistical significance is indicated by bold type ($p < 0.01$) or underlining ($p < 0.05$). All sites had measurements from at least ten years within the period from 1980 through 1999.

Site	CO	NO _x	Ozone	PM ₁₀	PM ₁₀ NO ₃	TSP	TSP NO ₃	CoH
Azusa	-2.28	-1.21	-1.72	-2.61	-1.03	-1.85	-1.47	
	0.33	0.26	0.47	0.60	0.82	0.43	0.38	
Fremont	-3.30	-1.28	<u>0.81</u>	-3.25	-5.31	-2.02	<u>-1.91</u>	-3.85
	0.41	0.46	0.39	0.95	1.77	0.63	0.78	0.57
Livermore	-2.14	-0.76	1.50	-3.63	-5.18	-1.83	-0.52	-4.17
	0.46	0.49	0.46	0.70	1.23	0.54	0.95	1.14
Napa	-2.11	-2.97	1.38	-5.92	-6.37	-1.50	-1.16	-6.96
	0.50	0.54	0.42	0.75	1.19	0.48	0.84	0.87
Riverside	-2.57	-2.07	<u>-1.17</u>	-2.95	-3.63	-2.20	-2.78	
	0.44	0.42	0.56	0.63	0.90	0.42	0.52	
San Bernardino	-5.05	-1.56	<u>-2.06</u>	-3.31	-1.77	-2.78	<u>-2.66</u>	
	0.56	0.52	0.99	0.75	1.22	0.80	1.08	
Visalia	0.01	-0.46	-0.94	-4.05	<u>-3.85</u>	-0.50		-3.23
	0.65	0.52	0.56	0.85	1.61	1.55		0.67

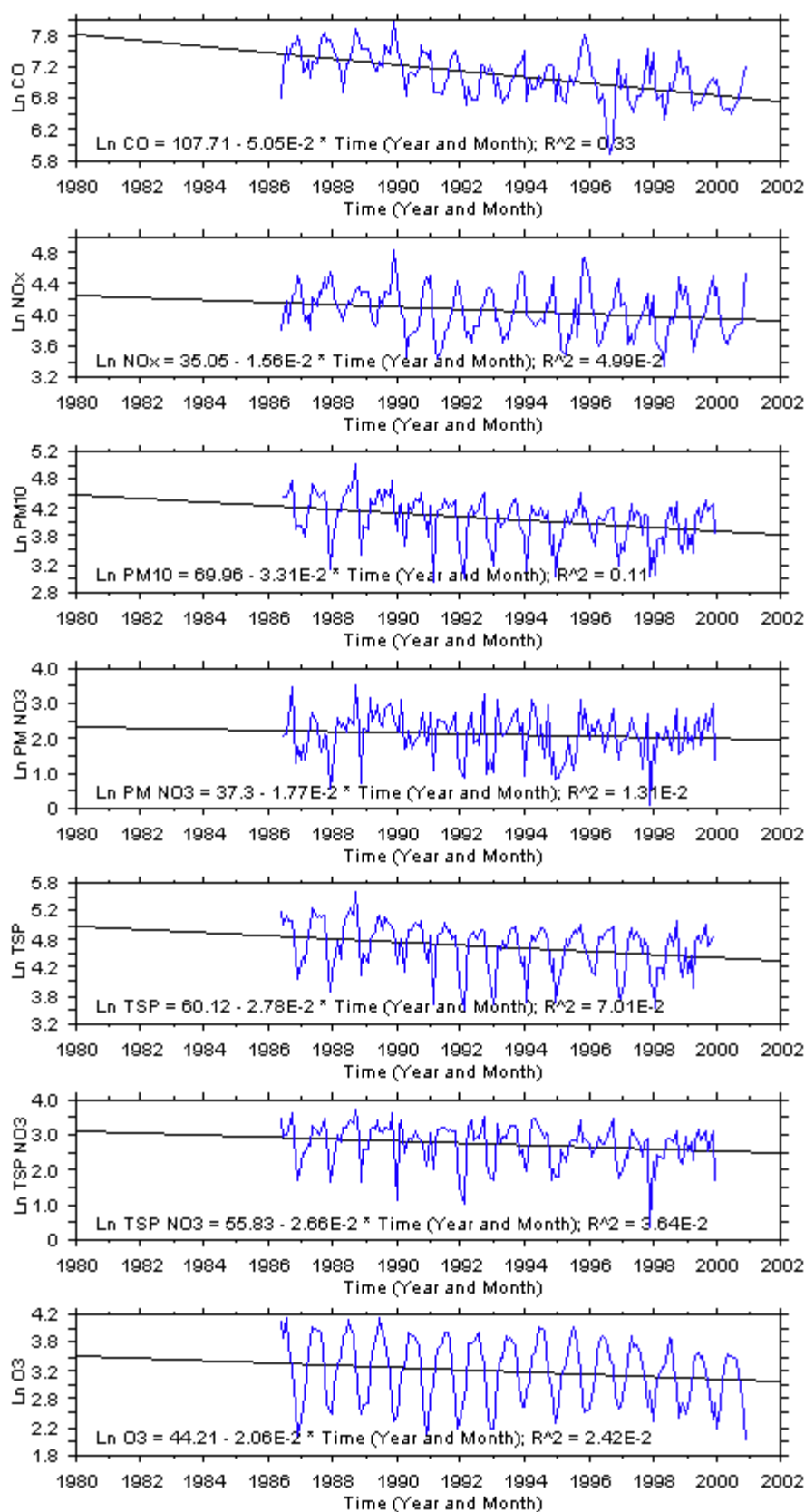


Figure 14. Time series of monthly average pollutant concentrations at San Bernardino. All data shown met the completeness criteria described in the text.

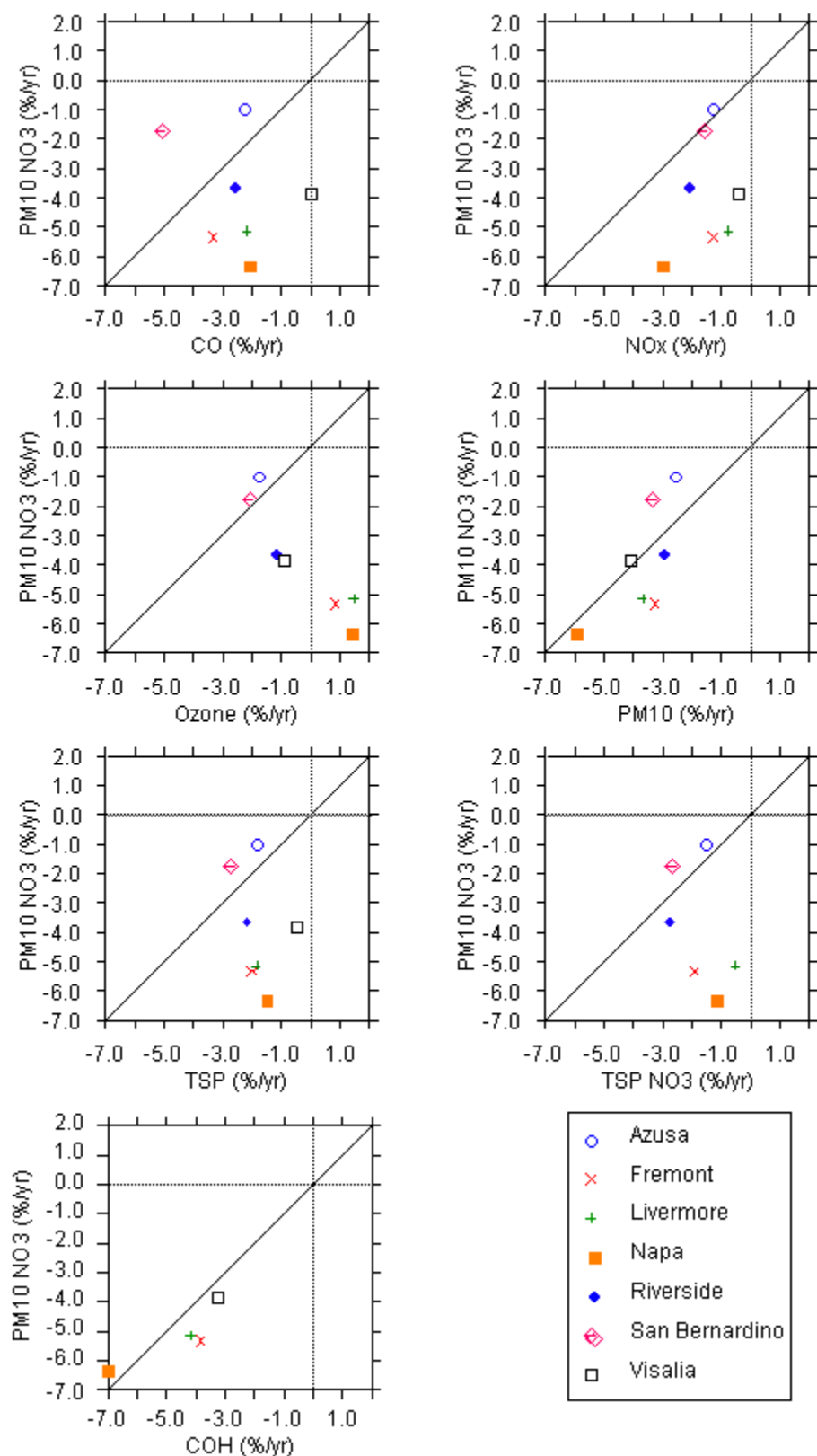


Figure 15. Comparison of PM₁₀ nitrate trends with trends in other pollutants at seven long-term monitoring sites. All sites had measurements spanning at least ten years within the period from 1980 through 1999.

Trends in Temperature and Precipitation

Monthly average temperatures measured at Los Angeles show clear seasonality and apparent longer-term cycles, or variations (Figure 16). Lower mean temperatures occurred during the years 1986 through 1994 and again beginning about 1999 when compared with the intervening years or with 1980 through 1985.

Monthly precipitation amounts also displayed seasonality and long-term variations (Figure 17). Precipitation amounts are typically near zero in most of the state during California's warm season (April through September), so the long-term precipitation variations pertain to the cool months. The precipitation trends were not uniform across sites, but generally the years 1985 through 1991 had lower average precipitation than did earlier or later years. Typically, higher precipitation amounts are associated with warmer wet seasons (El Ninos are associated with warmer ocean temperatures).

The seasonal variations of temperature may be directly incorporated into a statistical model using monthly-average temperature records, or they may be included using sine and cosine terms (Figure 18). Figure 18 shows that periodic functions of month provide a good representation of seasonal variations of temperature, so that either actual temperature records or a statistical representation may be used. The long-term temperature variability, which is evident in Figure 16, is not accounted for with the simple sine and cosine terms, but again may be included in a statistical model either directly using temperature records or indirectly using additional sine and cosine terms with multi-year periodicities. However, as indicated in Figure 18, the long-term variations of temperature (temperature anomalies) are small in comparison with the seasonal variation of approximately 15 degrees F.

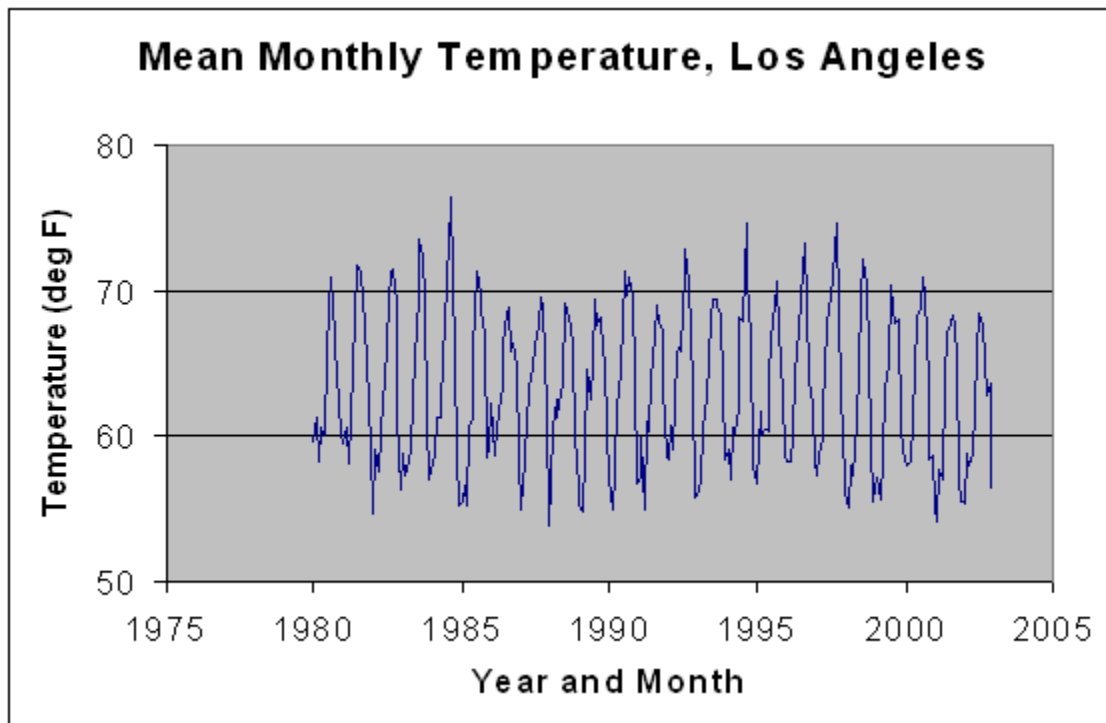


Figure 16. Monthly average temperature at Los Angeles.

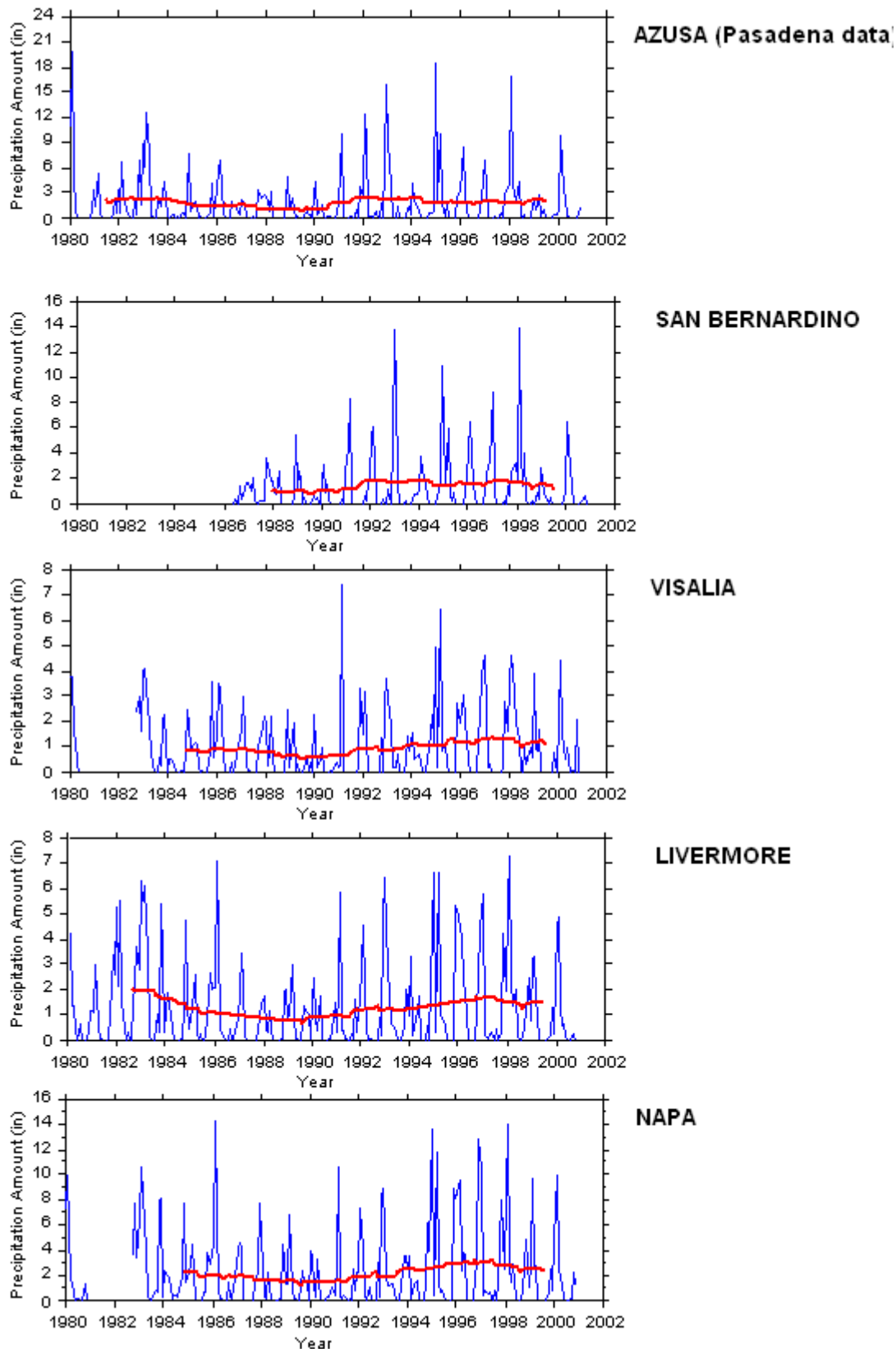


Figure 17. Monthly precipitation amounts at Azusa, San Bernardino, Visalia, Livermore, and Napa for 1980-2001. The 3-year moving average is superimposed. Precipitation amounts measured at Pasadena were used for Azusa.

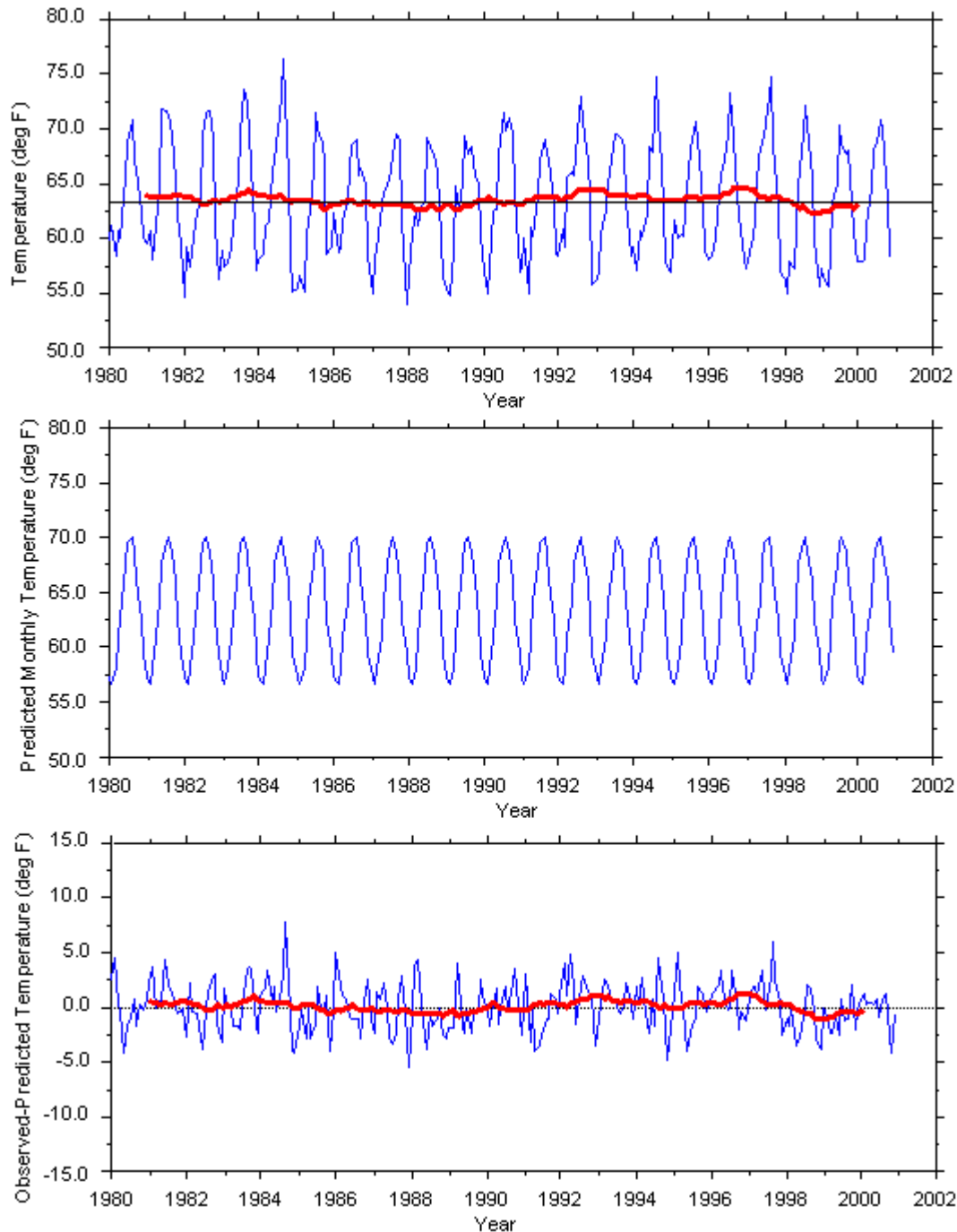


Figure 18. Comparison of monthly average temperature in Los Angeles with a periodic function of month. The differences between the measured temperatures (top) and the temperatures predicted from a periodic function (center) are shown in the bottom panel. Two-year moving averages have been superimposed on the monthly averages of the measured temperatures and their deviations from the periodic function. The moving-average series each show small deviations from their series means and no long-term trend.

Variations of temperature, relative humidity, and precipitation amount are known to affect ambient pollutant concentrations. Particulate nitrate formation, for example, is favored under cooler temperatures and higher relative humidity. Particulate matter concentrations are subject to washout, and so may decline when precipitation amounts are high. In California, clean marine air often follows the passage of a frontal system, causing ambient pollutant levels to decline dramatically. When pollutant trends are examined, variations of temperature, relative humidity, and precipitation amount may be found to influence average pollutant levels. Thus, incorporating these influences into a statistical model may improve the accuracy of trend estimates. In the next section, we incorporate seasonal and multi-year variations of temperature, humidity, and precipitation into a statistical model. The effects on the estimates of trends are then discussed.

Long-term Pollutant Trends - Graphical Analysis

All sites showed nonlinear trends in all the species that were examined (Figures 19 through 25). As observed in the linear regressions, NO_x , PM_{10} mass, TSP mass, PM_{10} nitrate, and TSP nitrate declined over time, usually showing some short-term (four to six year) variations superimposed on a general downward trend. At some sites, particularly Visalia, concentrations of one or more species rose until about 1991 before declining. Note that the figures show both the monthly averages and the three-year moving averages. The monthly averages exclude months failing to meet completeness criteria except as noted, whereas the three-year moving averages include all months (computation of moving averages is complicated by missing months).

At all sites, the moving averages indicate that one or more of the pollutants tended to show less change during the 1980s and to decrease more during the 1990s. TSP records are shorter for some sites than others, and PM_{10} measurements did not begin until the mid 1980s, so the contrasts between the 1980s and 1990s are not always evident. Nonetheless, all sites show lower levels of PM_{10} mass and nitrate during the 1990s than from 1985 to 1990. These ambient trends are consistent with estimates of historical NO_x emissions (Table 7) but not with estimates of PM_{10} emissions (Table 8). In the South Coast, San Joaquin, and San Francisco Bay Area Air Basins, NO_x emissions showed more substantial declines during the 1990s than during the 1980s. However, estimated PM_{10} emissions showed no declines. Therefore, the observed trends in TSP and PM_{10} mass may be due to trends in meteorological factors (e.g., precipitation amount) or to trends in secondary PM concentrations (principally, sulfate and nitrate). Alternatively, emissions estimates may not represent the emission changes that actually occurred.

Studies of $\text{PM}_{2.5}$ composition in the South Coast Air Basin show that secondary species (sulfate, nitrate, and ammonium) constituted approximately 40 percent of the fine mass, and exhibited declining mean concentrations from 1982 to 1993 (Christoforou et al., 2000). Lacking complete speciation for the routine measurements, we estimated how much of the TSP and PM_{10} mass was due to primary components as $\text{primary mass} = \text{mass} - \text{sulfate} - \text{nitrate} - \text{ammonium}$. At the seven long-term sites, the estimated primary TSP declined by 1.9 to 3.0 percent per year. The estimated primary PM_{10} declined by 2.4 to 4.8 percent per year. These declines are

comparable to the declines in TSP mass and PM_{10} mass listed in Table 6. Thus, the observations indicate that declining ambient concentrations of PM mass and TSP mass are not due entirely to declines in secondary species; primary PM and TSP have also declined. In contrast, the estimates of primary PM emissions show no decline. This discrepancy between the trends shown by ambient measurements and emissions estimates warrants further analysis.

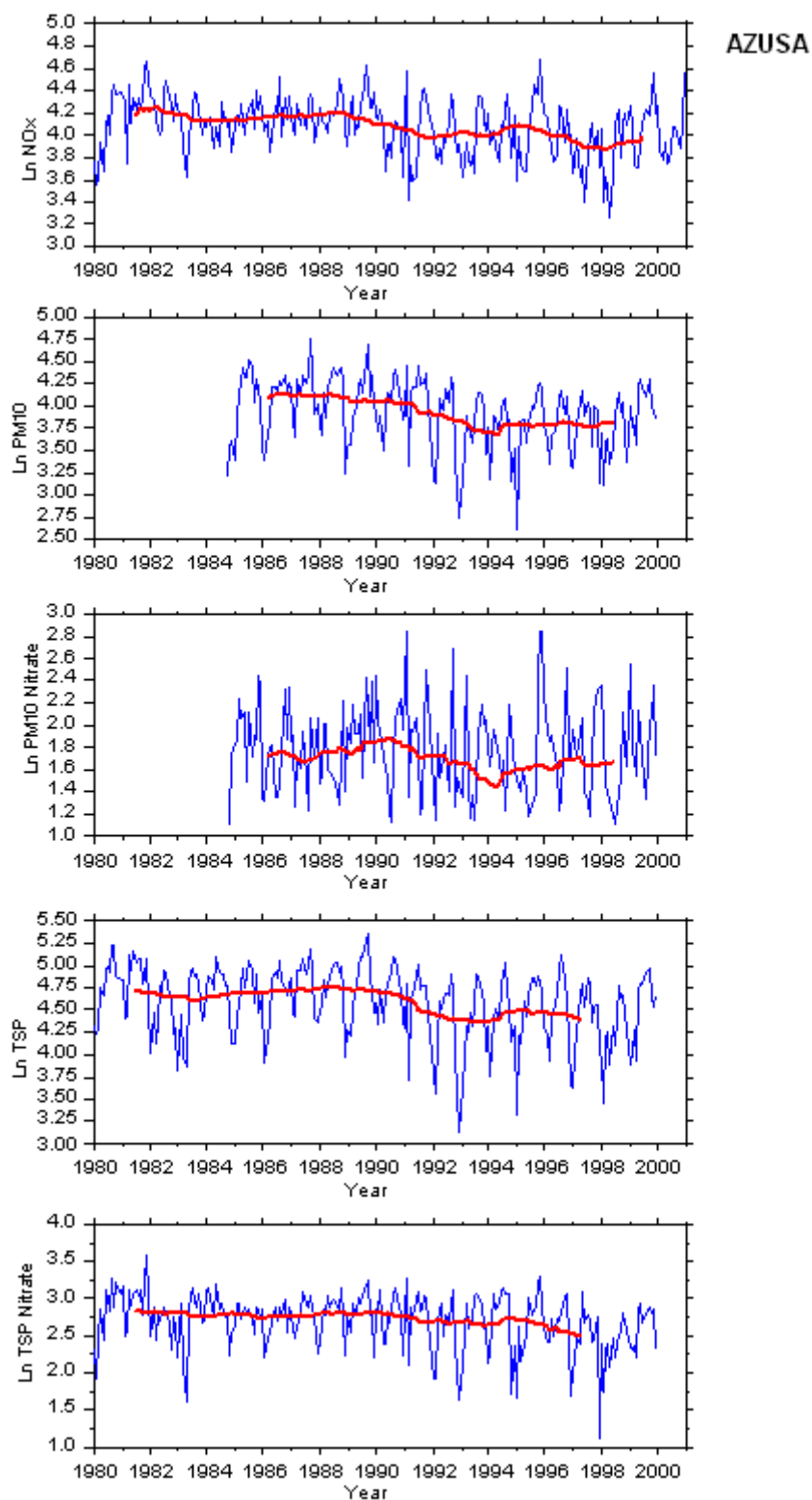


Figure 19. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP and TSP nitrate concentrations at Azusa during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

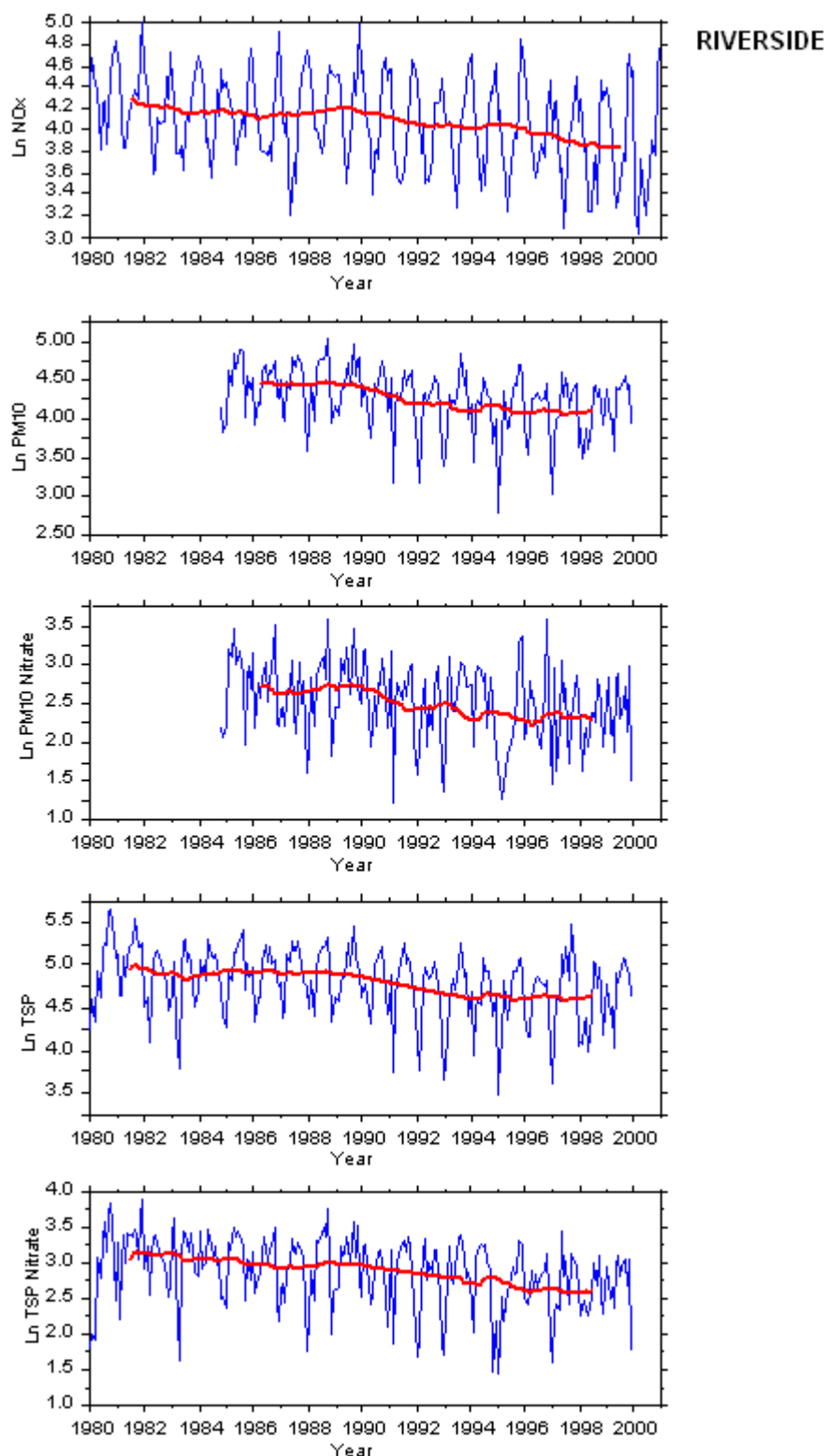


Figure 20. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP, and TSP nitrate concentrations at Riverside during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

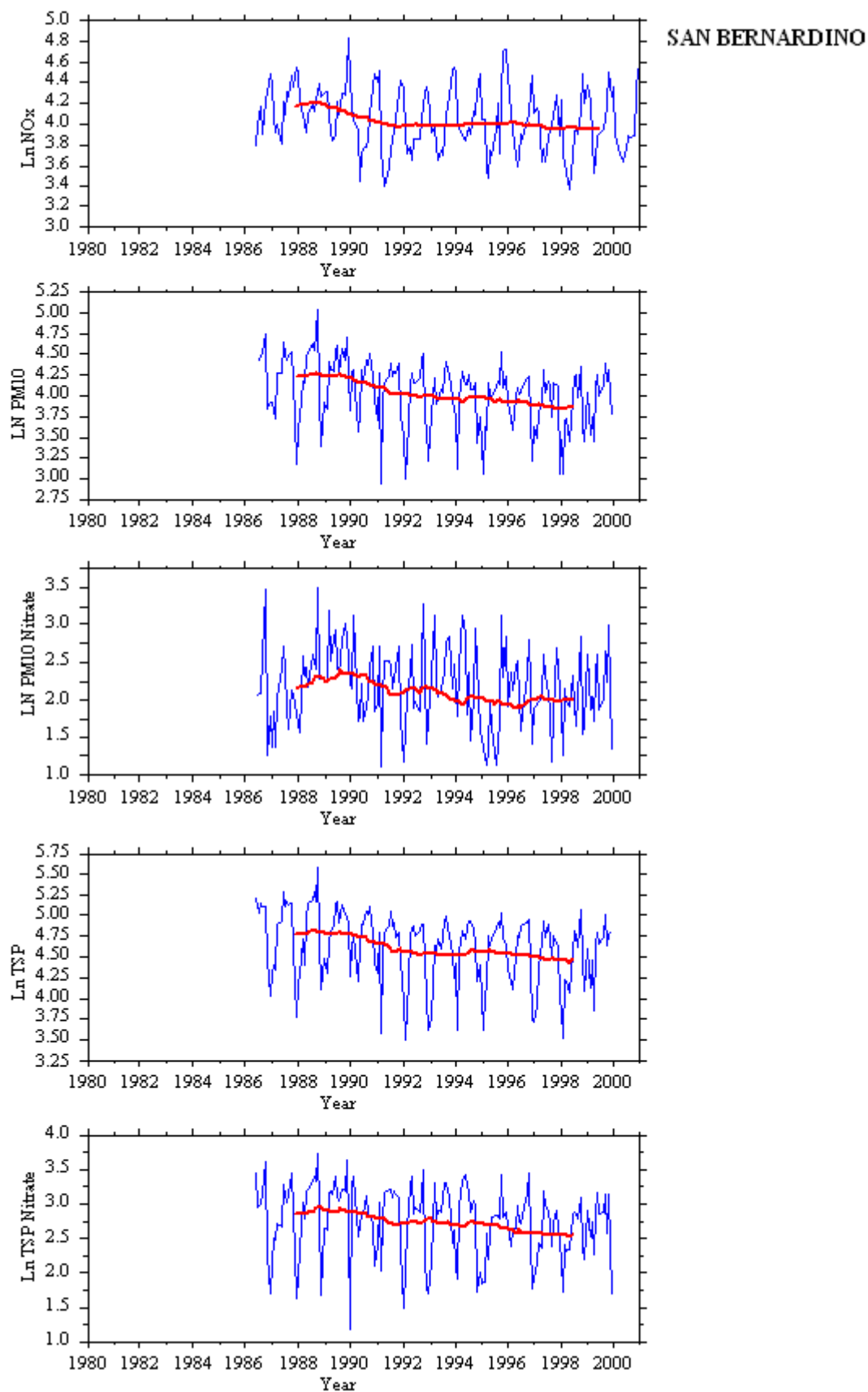
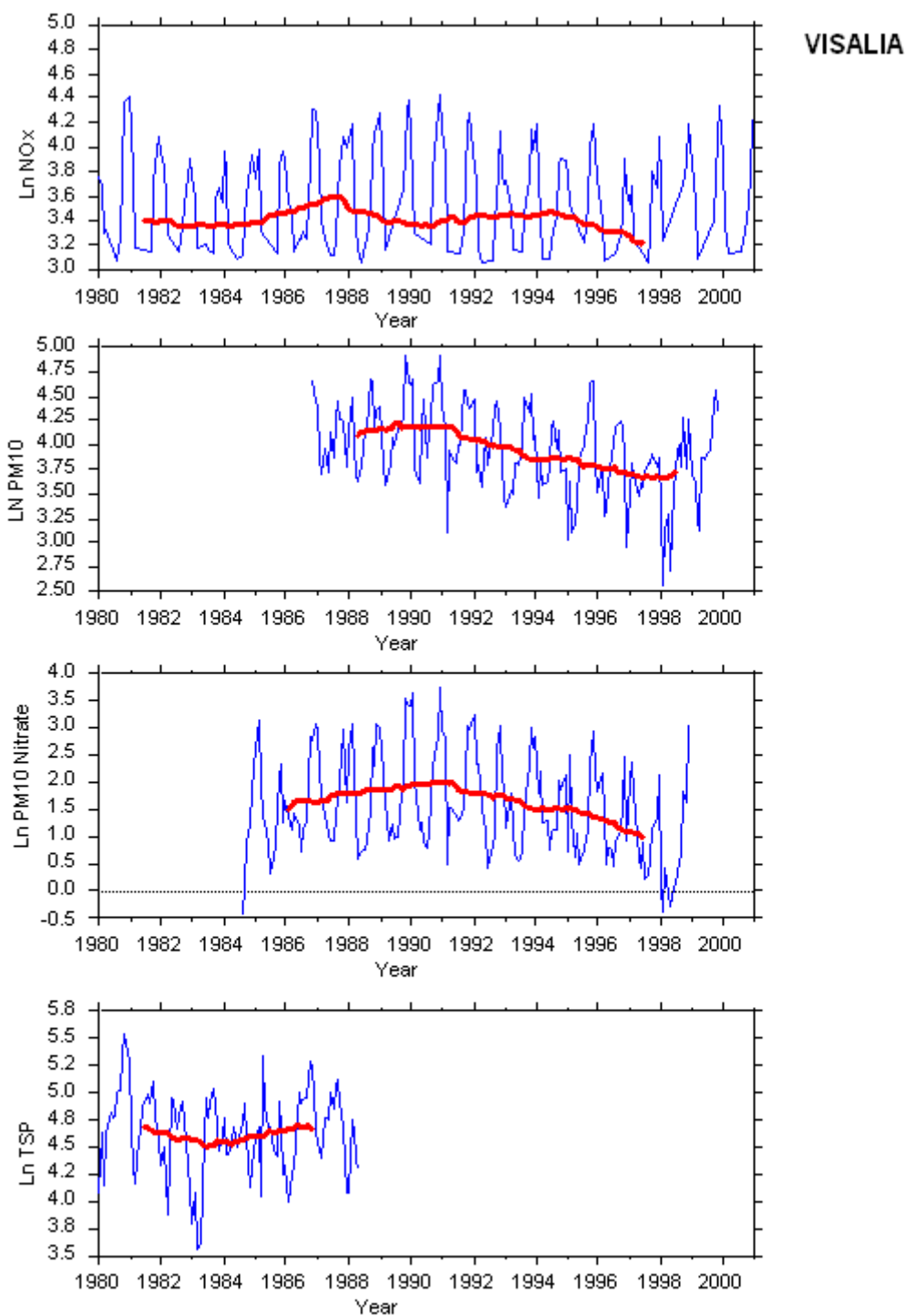


Figure 21. Natural log of monthly-average NO_x , PM_{10} , PM_{10} nitrate, TSP, and TSP nitrate at San Bernardino during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.



TSP Nitrate data unavailable for Visalia

Figure 22. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP, and TSP nitrate at Visalia during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

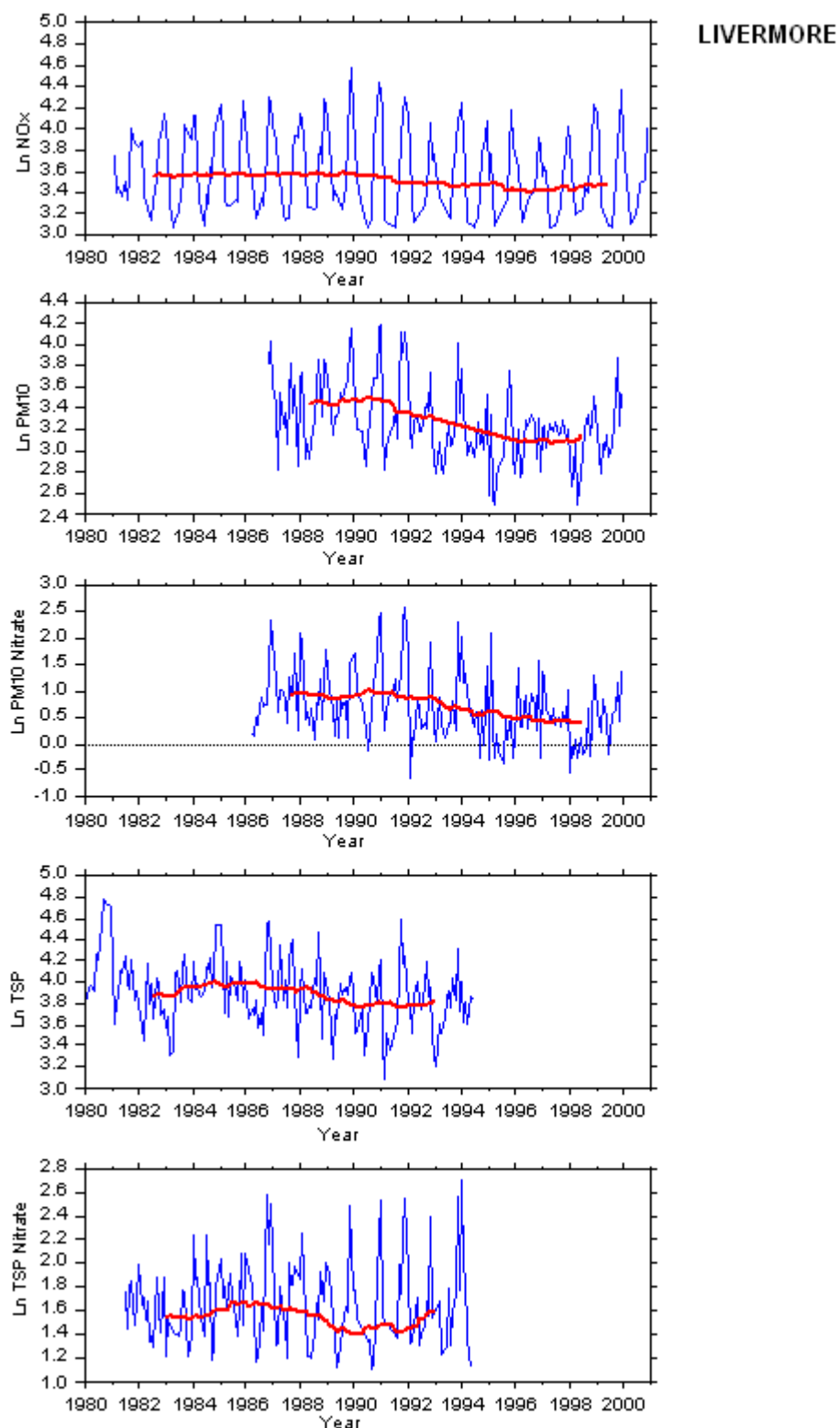


Figure 23. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP, and TSP nitrate at Livermore during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

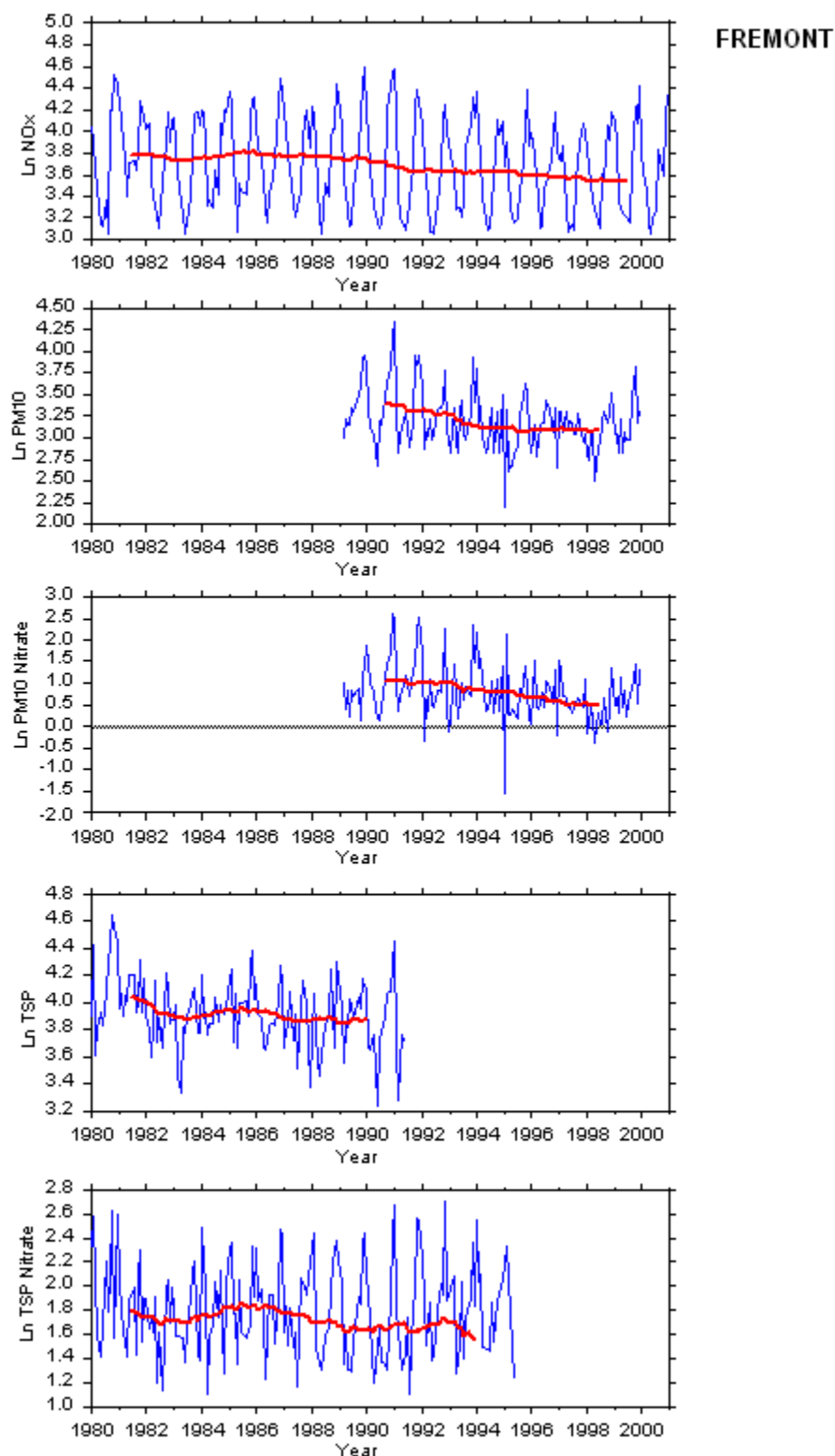


Figure 24. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP, and TSP nitrate at Fremont during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

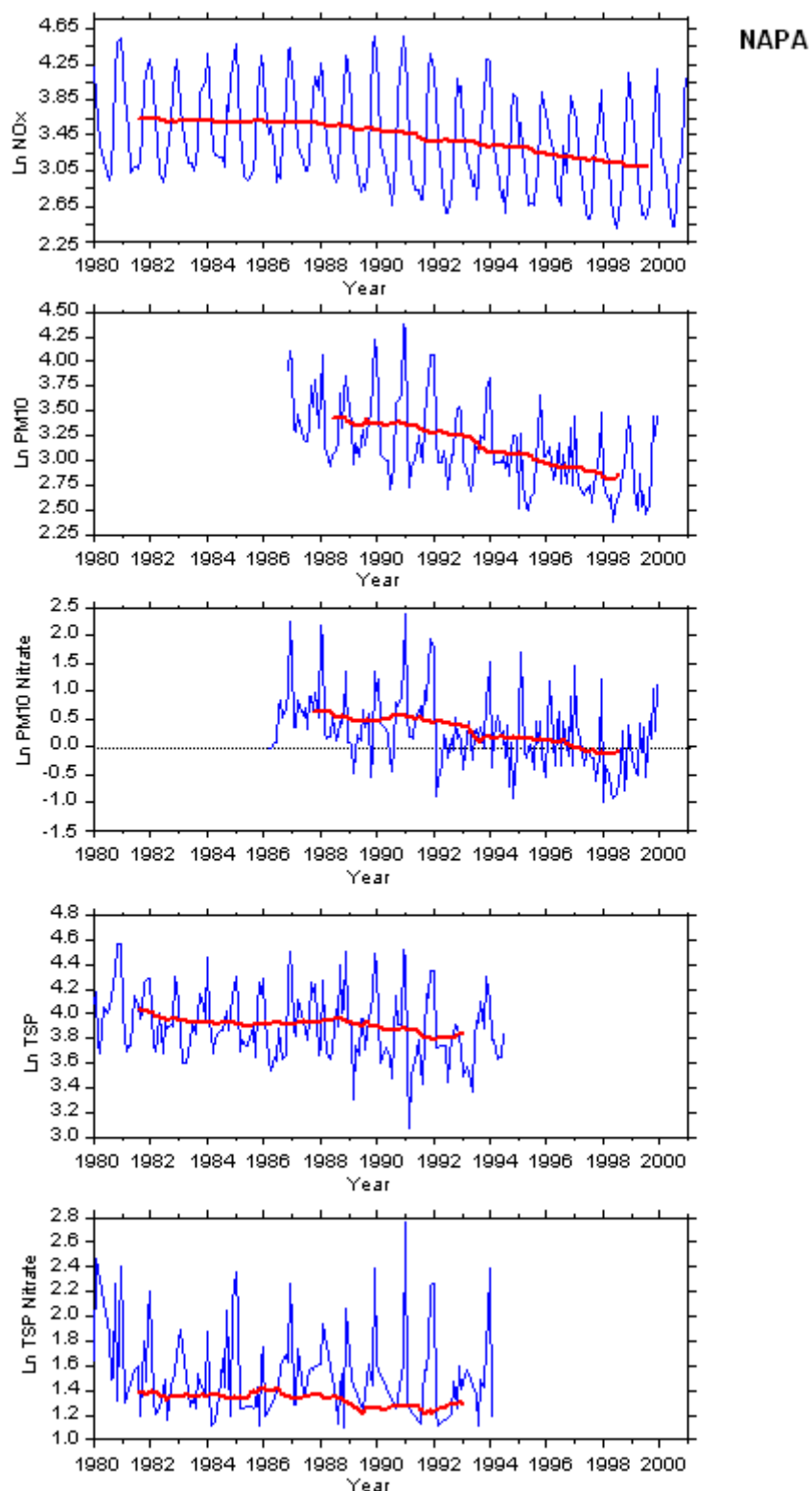


Figure 25. Natural log of monthly-average NO_x, PM₁₀, PM₁₀ nitrate, TSP, and TSP nitrate at Napa during the years 1980-2000. The 3-year moving average is superimposed. Units are ppbv for NO_x and $\mu\text{g m}^{-3}$ for other compounds.

Table 7. Estimated emissions of NO_x in the South Coast, San Joaquin Valley, and San Francisco Bay Area air basins, 1980-2000. Units are tons per day. Source: Alexis et al., 2001.

Year	South Coast	San Joaquin Valley	San Francisco Bay
1980	1780	801	808
1985	1923	809	755
1990	1780	791	756
1995	1473	688	659
2000	1208	596	558

Table 8. Estimated emissions of PM₁₀ in the South Coast, San Joaquin Valley, and San Francisco Bay Area air basins, 1980-2000. Units are tons per day. Source: Alexis et al., 2001.

Year	South Coast	San Joaquin Valley	San Francisco Bay
1980	311	449	154
1985	341	452	159
1990	367	456	165
1995	339	447	166
2000	357	474	167

Warm and Cool Seasons

Mean ambient concentrations differed between warm and cool seasons at all sites, though the seasonal patterns were not identical at all sites (Figures 26 through 32). These figures show that:

- NO_x levels were highest during winter months (January - March and October through December) at all sites except Azusa (which showed no differences between winter and summer NO_x levels);
- PM_{10} mass concentrations were greatest during summer months at the three sites in southern California. They were greatest during winter months at the San Joaquin and Bay area sites. Three of the latter four sites began showing roughly comparable winter and summer PM_{10} mass levels beginning between 1991 and 1995.
- PM_{10} nitrate levels were either greater during winter (Azusa, Visalia, Livermore, Fremont, and Napa) or nearly the same between winter and summer (Riverside and San Bernardino). Since 1995, Fremont and Napa have shown roughly equal mean summer and winter PM_{10} nitrate levels.
- TSP mass was greater during summer months at the sites in southern California and the San Joaquin Valley. In the Bay area, winter and summer TSP mass levels were comparable at Livermore and Fremont, while Napa showed higher winter TSP mass concentrations.
- TSP nitrate concentrations were greater during summer months at the sites in southern California, but were greater during winter months at sites in the Bay area.

Trends are evident during both winter and summer months for all species at most sites. As previously noted, Azusa appears to be something of an exception in showing winter PM_{10} nitrate levels that become progressively greater than summer concentrations (Figure 26). The other long-term sites show declining nitrate levels during both winter and summer.

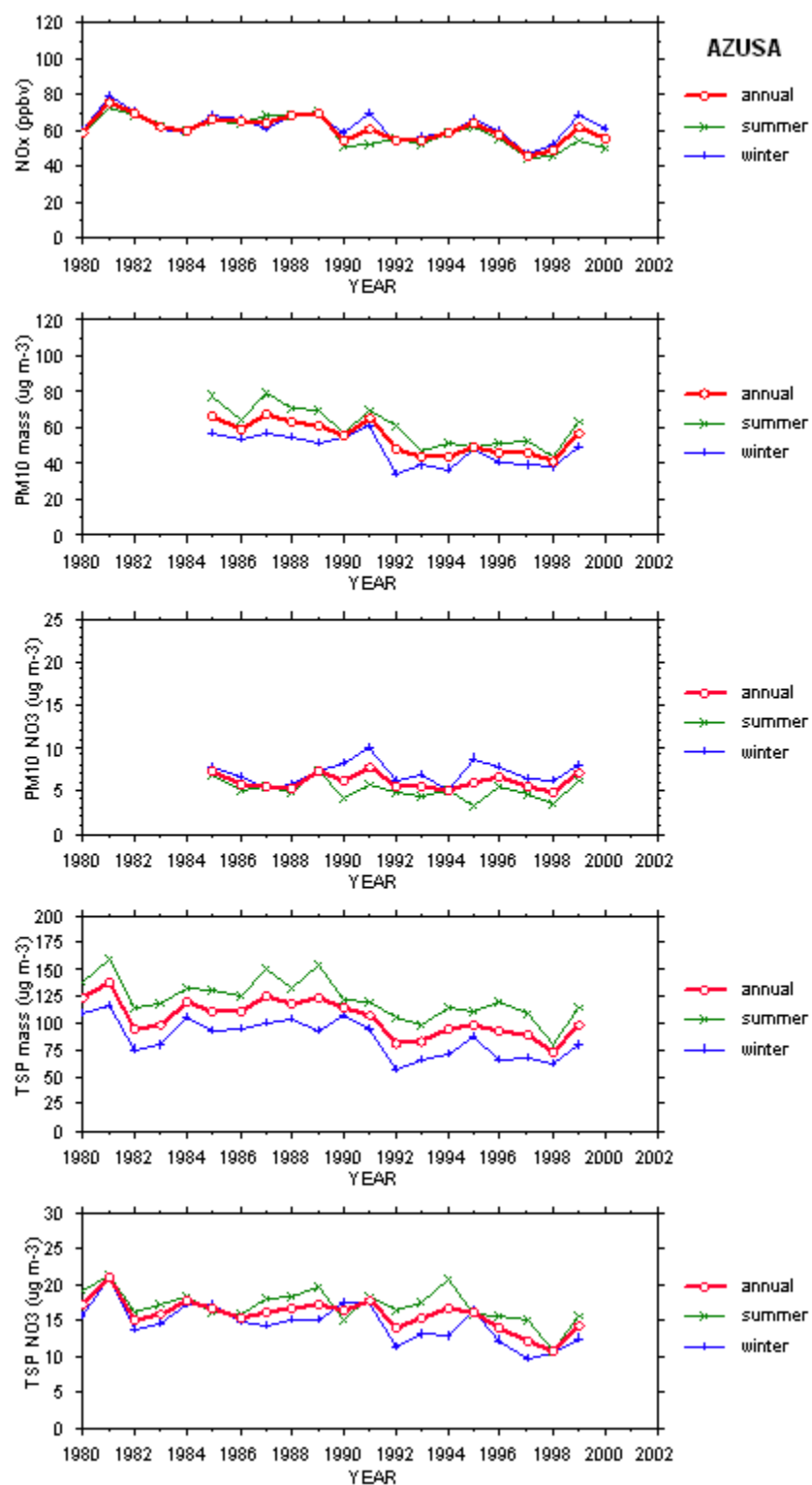


Figure 26. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Azusa for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

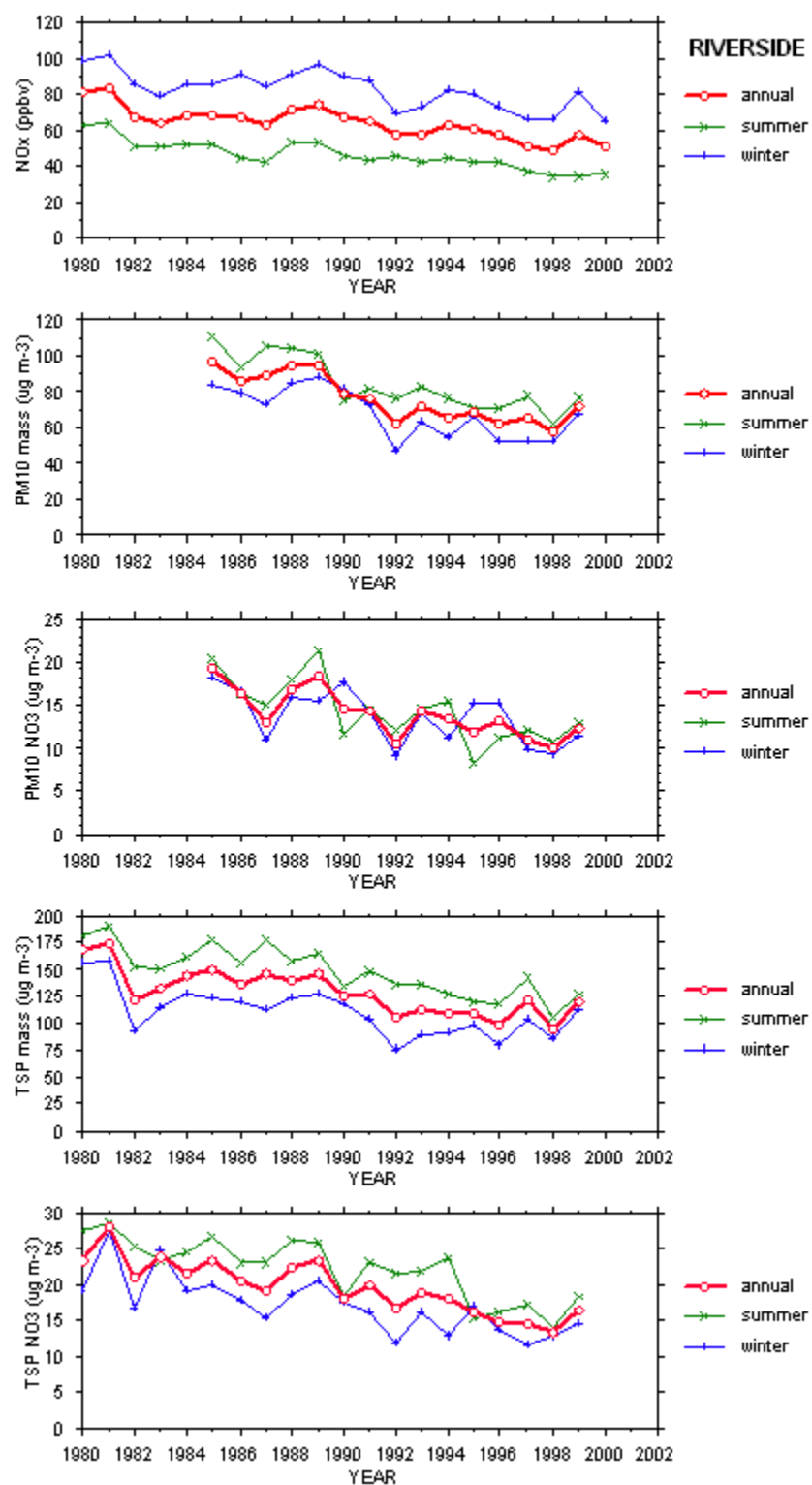


Figure 27. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Riverside for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

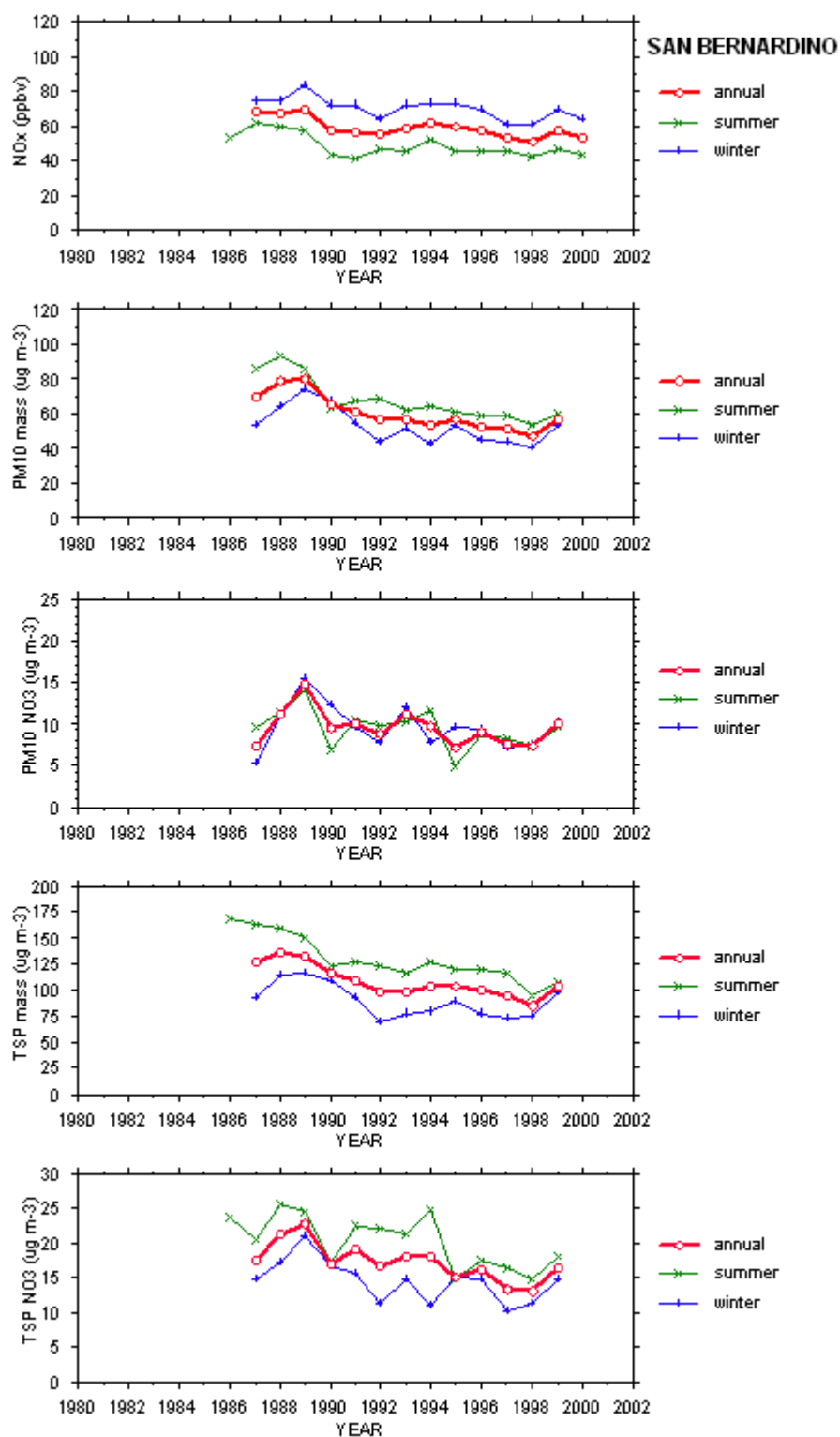


Figure 28. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at San Bernardino for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

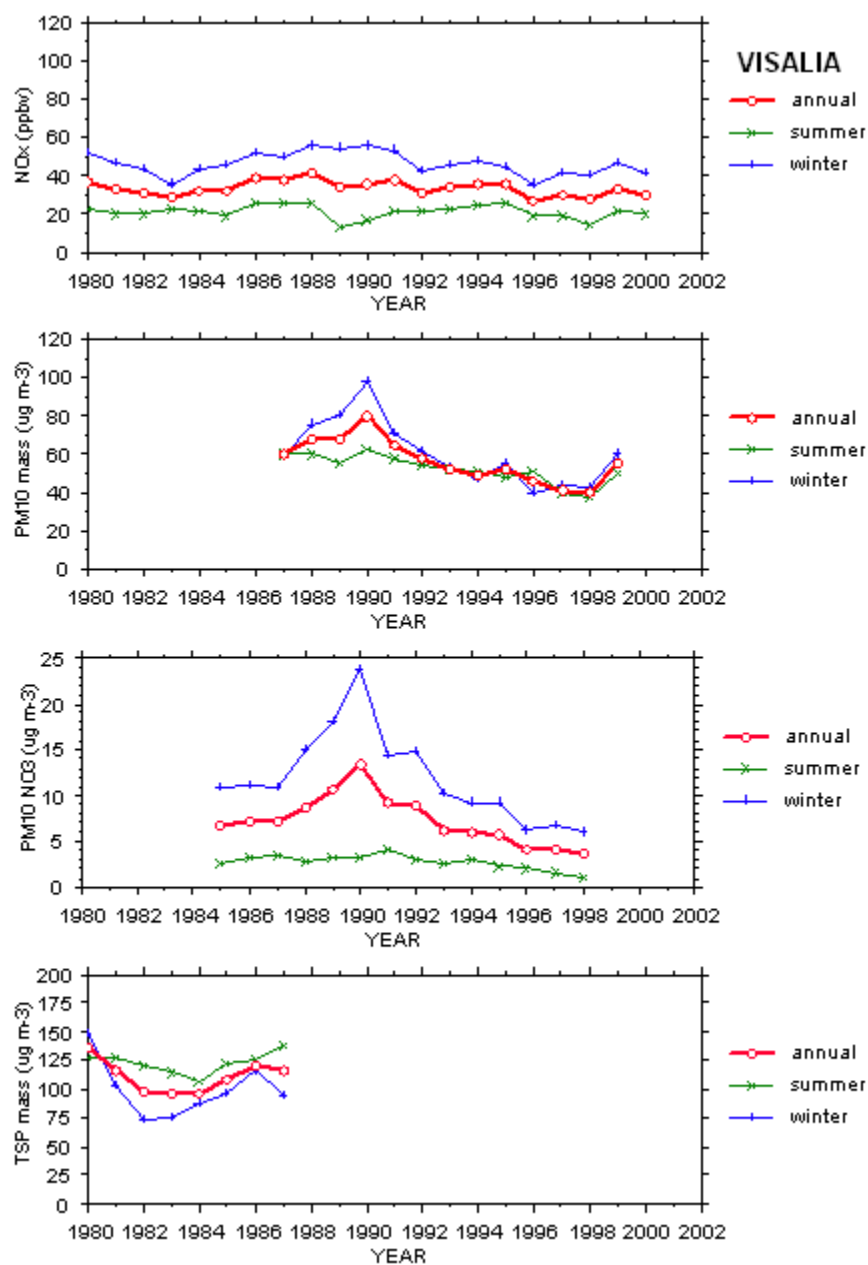


Figure 29. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Visalia for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

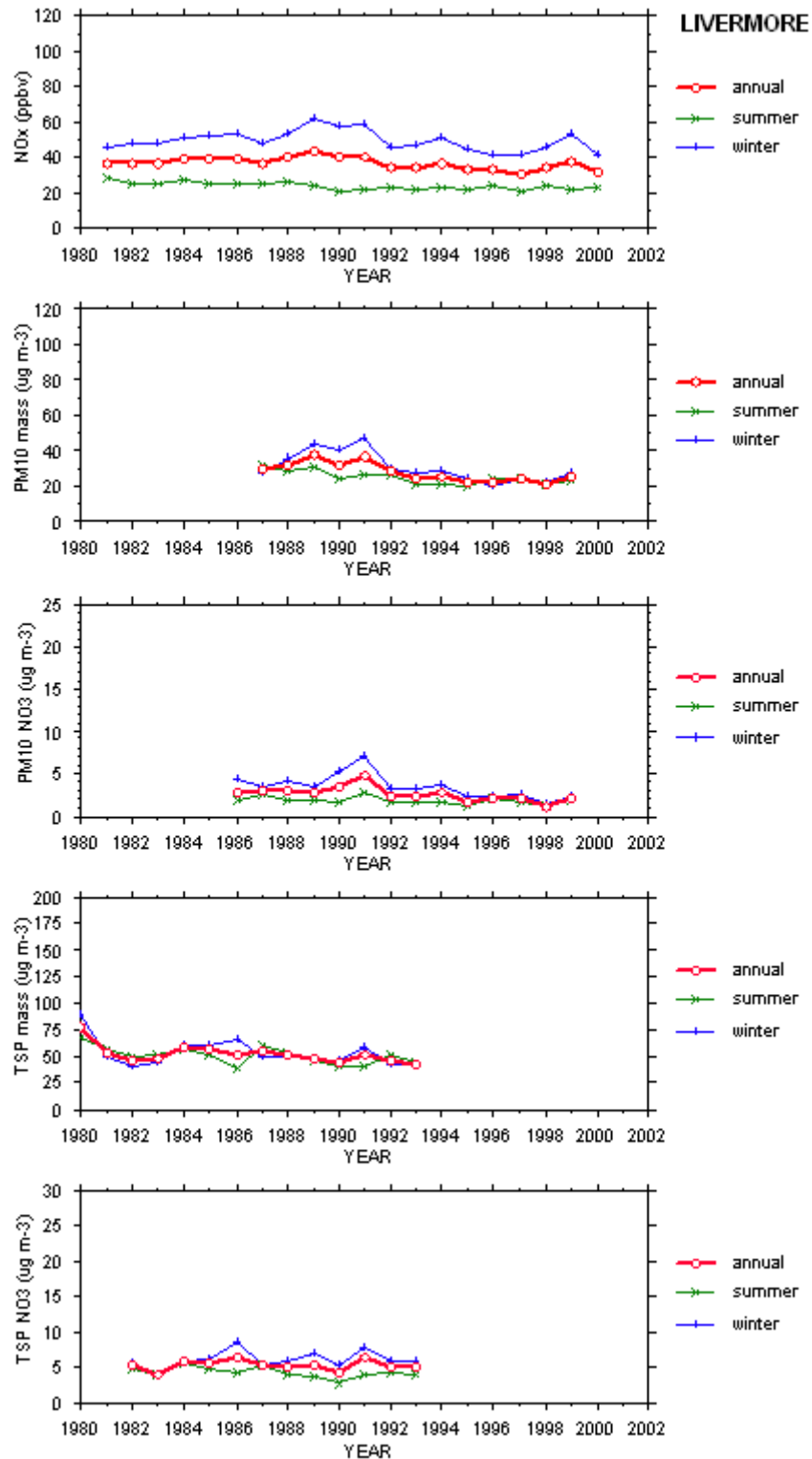


Figure 30. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Livermore for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

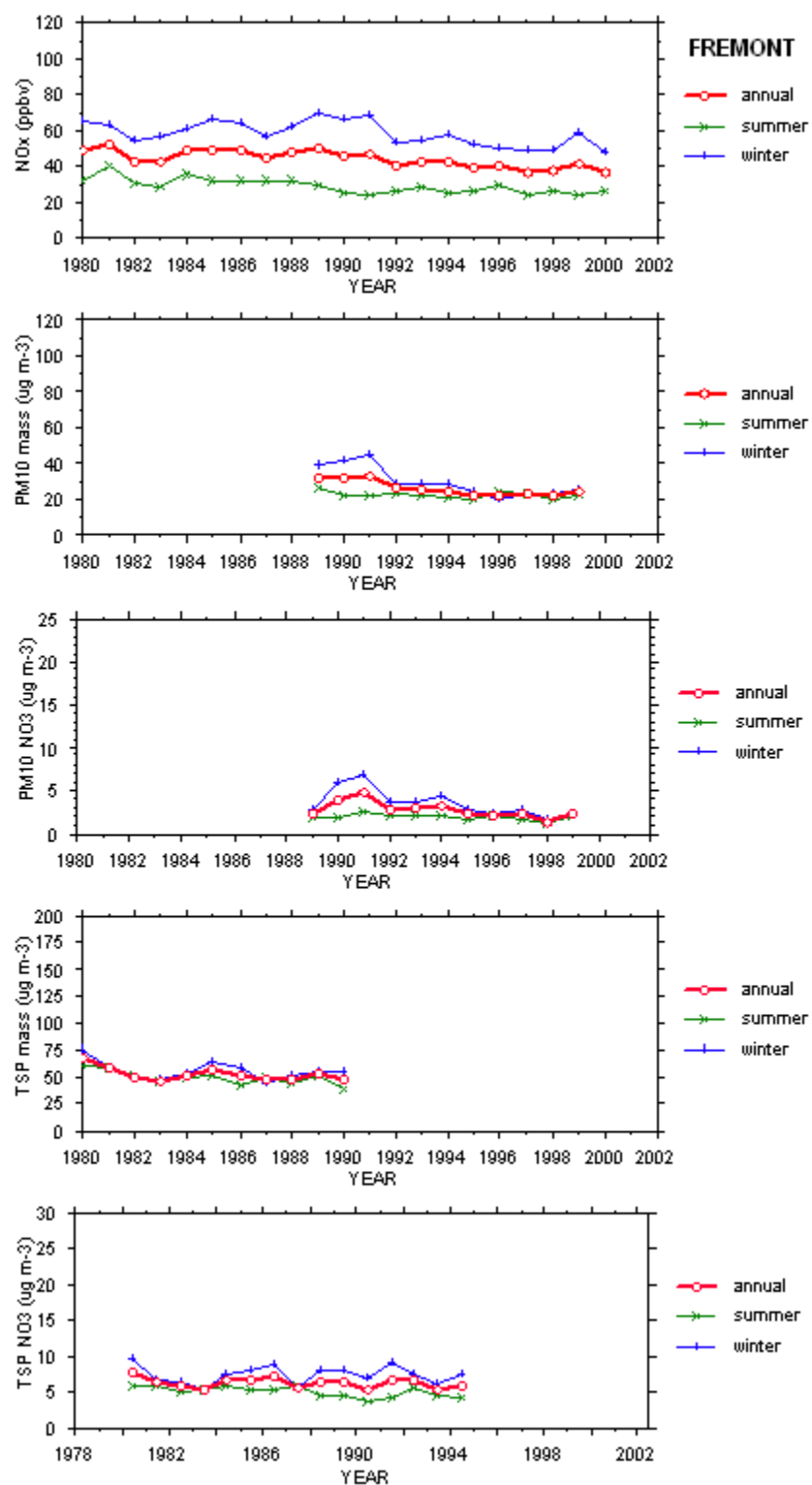


Figure 31. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Fremont for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

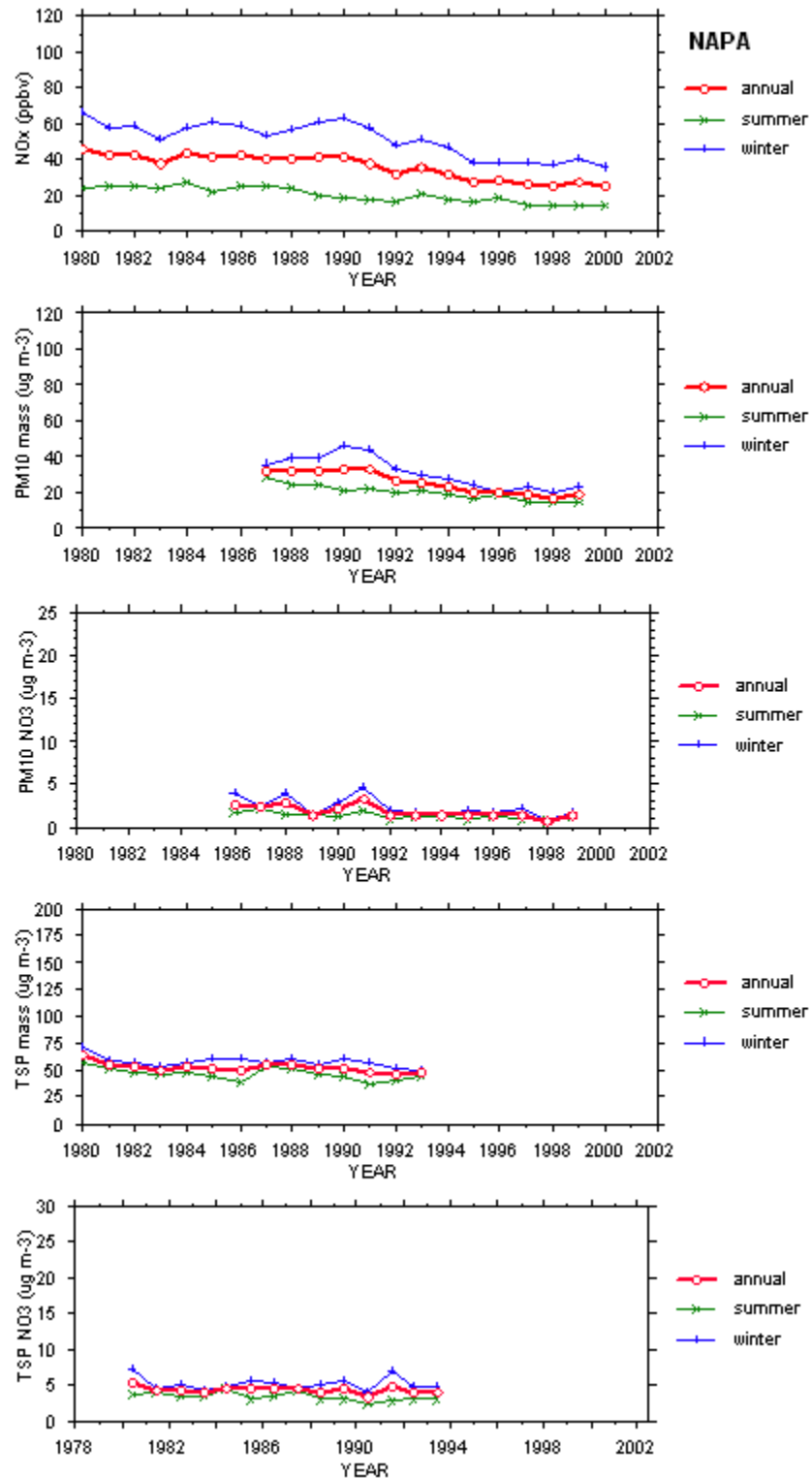


Figure 32. Annual, summer, and winter averages of PM₁₀ mass, PM₁₀ nitrate, TSP mass, TSP nitrate, and NO_x at Napa for the period 1980-2000. Summer months are April through September and winter months are January through March and October through December.

Trends in Ambient Concentrations of CO, Coefficient of Haze, and NMHC

As previously noted, measurements of CO, coefficient of haze (CoH), and nonmethane hydrocarbon (NMHC) concentrations were obtained and monthly averages were computed. Not all seven long-term sites had each of these measurements. Trends were evident for both CO (Figures 33 and 34) and CoH (Figure 35), with CoH especially declining during the 1990s. Note that CO concentrations have been displayed on a logarithmic scale, consistent with the style used for monthly average pollutant concentrations in this report; CoH has been displayed in its original units, which are 1/1000 feet.

The record of NMHC measurements is too short to analyze reliably, commencing in 1990. The data suggest the occurrence of declining ambient levels beginning in 1995 or 1996 (Figures 36 and 37).

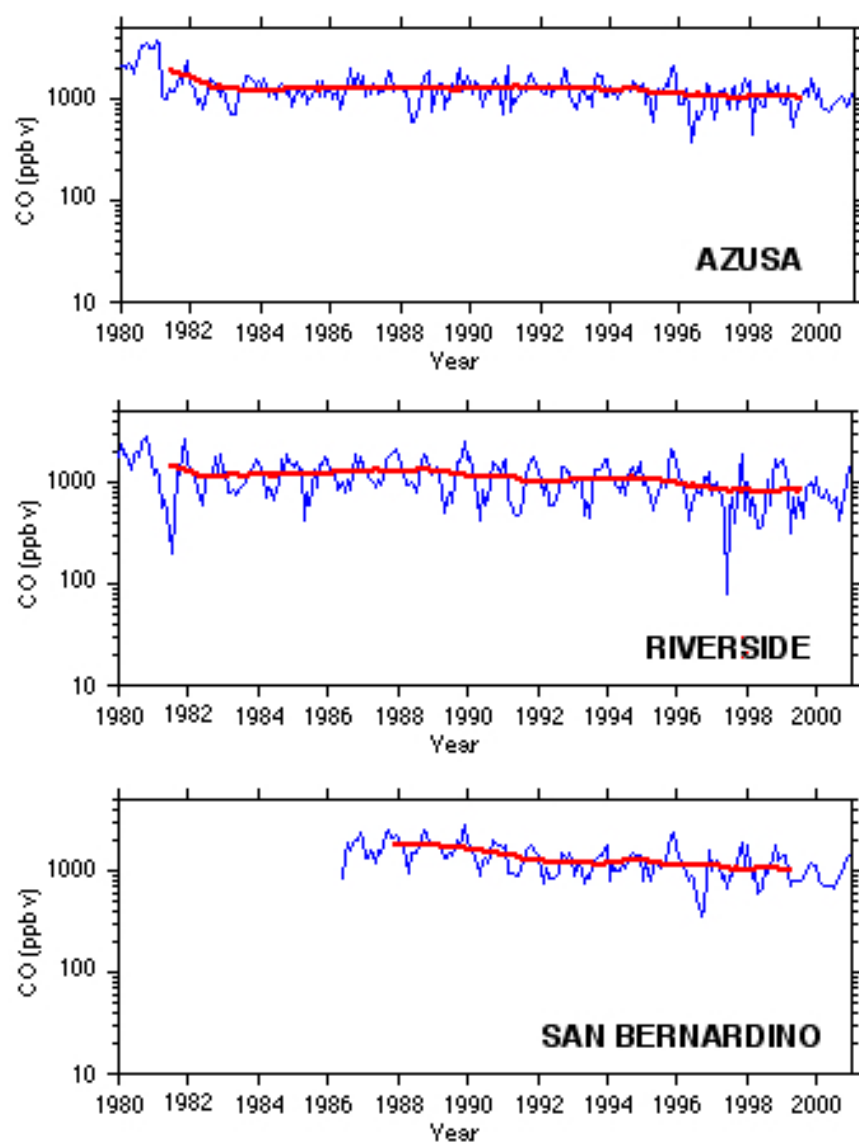


Figure 33. Monthly-average carbon monoxide at Azusa, Riverside, and San Bernardino during 1980-2000. The 3-year moving average is superimposed.

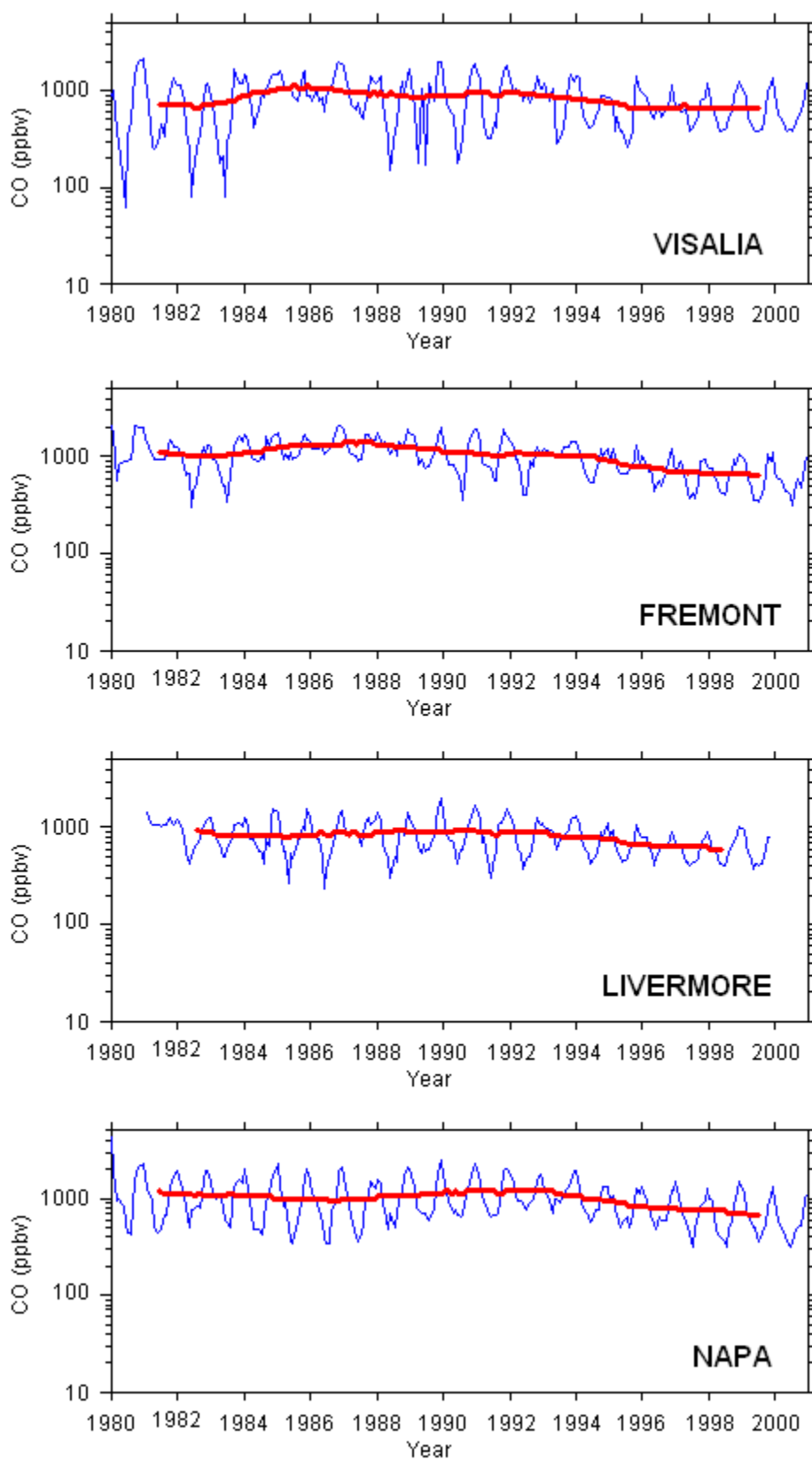


Figure 34. Monthly-average carbon monoxide at Visalia, Livermore, Fremont and Napa during 1980-2000. The 3-year moving average is superimposed.

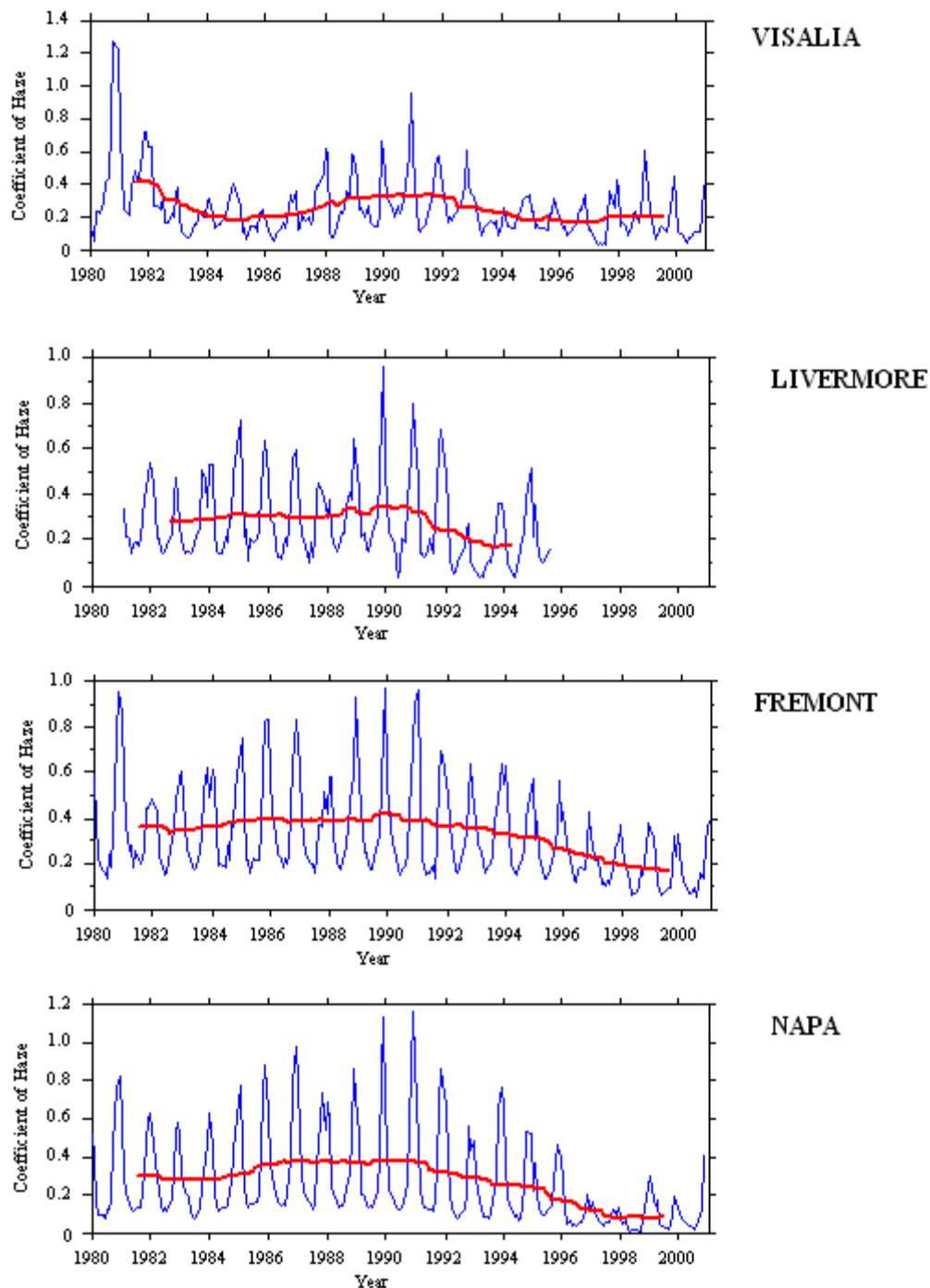


Figure 35. Monthly-average CoH during 1980-2000 at Visalia, Livermore, Fremont and Napa. The 3-year moving average is superimposed. Units of measurement are 1/1000 feet. Coefficient of haze is a measurement of optical attenuation due to absorption by particles. The principal absorbing species is elemental carbon.

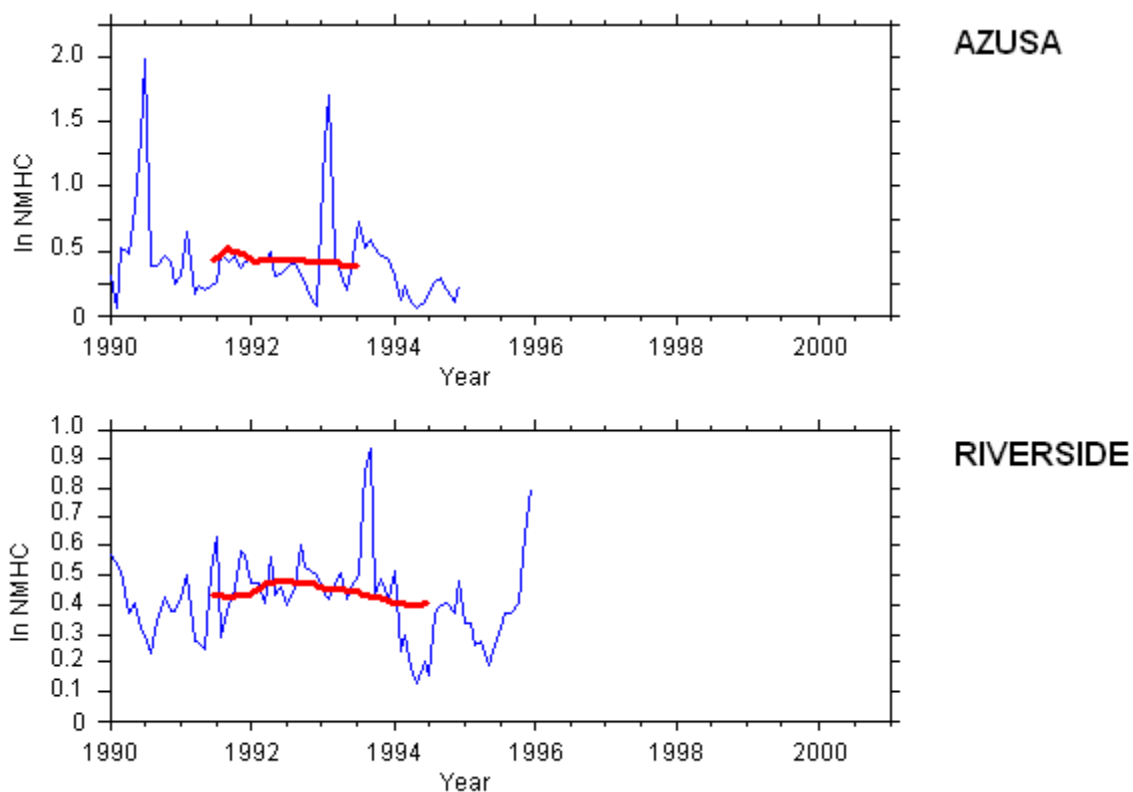


Figure 36. Natural log of monthly-average non-methane hydrocarbon concentration at Azusa and Riverside during 1990-2000. The 3-year moving average is superimposed.

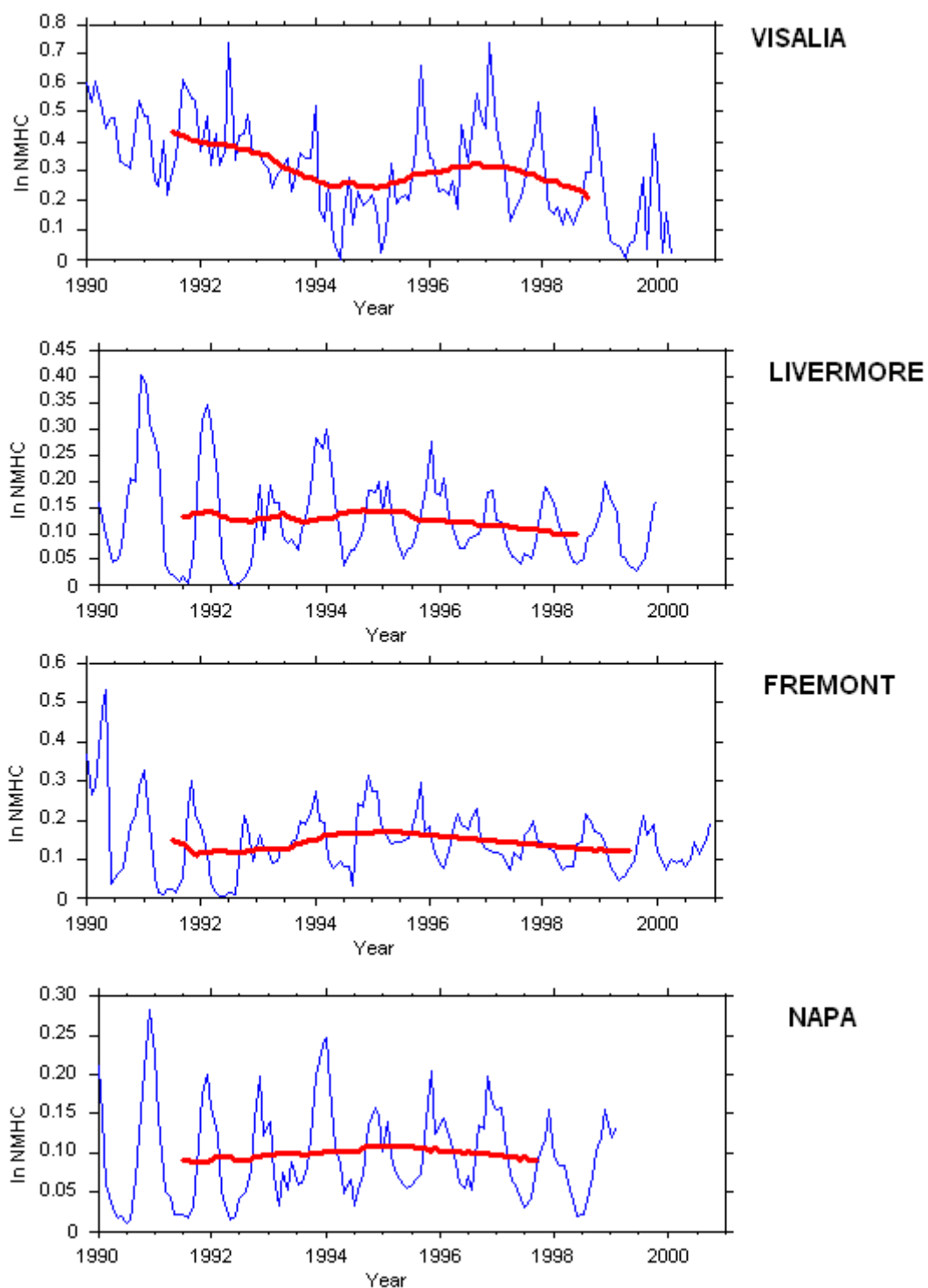


Figure 37. Natural log of monthly-average non-methane hydrocarbon concentration at Visalia, Livermore, Fremont and Napa during 1990-2000. The 3-year moving average is superimposed. Units of measurement are ppmC.

Stepwise Multiple Regression Results

For each site, stepwise multiple regression was used to develop a statistical model of the long-term behavior of each compound. The regressions related the compounds' log-transformed monthly averages to the following variables: (1) monthly average temperature and precipitation amount, (2) month (i.e., seasonal variation not already reflected in average monthly temperature and precipitation variations), (3) time (linear trend, possibly different for warm and cool seasons), (4) multi-year cycles (nonlinear long-term variations), (5) NO_x , CO, and CoH levels (used as predictor variables in the statistical models for PM_{10} and TSP nitrate, with possibly different relationships for warm and cool seasons). The completeness criteria discussed previously were applied to all monthly averages.

The stepwise multiple regressions were first compared with the simple regressions that were previously discussed (see Table 6), and the comparison is shown in Table 9 and Figure 38 (complete multiple regression results are listed later in Tables 10 through 16). For NO_x and PM_{10} mass, the trends determined from the multiple regressions were similar to those determined from the simple regressions, within the confidence limits of the regression slopes (Tables 6 and 9; Figure 38). In contrast, the multiple regressions for PM_{10} nitrate with temperature and precipitation included as predictors indicated smaller declines than did the simple regressions. Thus, changes in temperature and precipitation over the period of record affected the estimates of the magnitudes of the nitrate trends, though both simple and multiple regressions showed the existence of PM_{10} nitrate trends of greater magnitude than the NO_x trends at most of the sites (Figure 38).

Table 9. Comparison of simpler linear regression trend results with multiple regression trend results. Trends in NO_x, PM₁₀ mass, and PM₁₀ nitrate are summarized from Tables 6 and 10 through 16. The entries are expressed as percent per year changes (declines are negative). For PM₁₀ nitrate, multiple regression results are shown for the statistical models both with and without primary pollutants (NO_x, CO, and CoH) included as predictors. All sites had measurements from at least ten years within the period from 1980 through 1999.

Site	NO _x		PM ₁₀ mass		PM ₁₀ nitrate		
	Simple	Multiple	Simple	Multiple	Simple	Multiple (without primary)	Multiple (with primary)
Azusa	-1.2	-1.4	-2.6	-3.3	-1.0	None	-0.2**
Fremont	-1.3	-1.4	-3.3	-2.9	-5.3	-3.8	None
Livermore	-0.8	-0.9	-3.6	-4.2	-5.2	-3.1	None
Napa	-3.0	-3.1	-5.9	-5.2	-6.4	-5.2	None
Riverside	-2.1	-2.4	-3.0	-3.1	-3.6	-3.1	None
San Bernardino	-1.6	-1.5	-3.3	-3.7	-1.8	None	None
Visalia	-0.5	-1.0	-4.1	-4.5	-3.9	-2.9	None

** Cool season only.

For both simple and multiple regressions, the trends in PM₁₀ nitrate substantially exceeded trends in NO_x (Figure 38): in the simple regressions, the median NO_x trend was a decline of 1.3 percent per year, whereas the median PM₁₀ nitrate trend was a decline of 3.6 percent per year. For the multiple regressions, the median NO_x trend was a decline of 1.4 percent per year, whereas the median PM₁₀ nitrate trend was a decline of 3.1 percent per year. These differences indicate that declining NO_x levels alone were not responsible for the full magnitudes of the declining nitrate concentrations, because PM nitrate is not expected to show a greater than proportional response to NO_x.

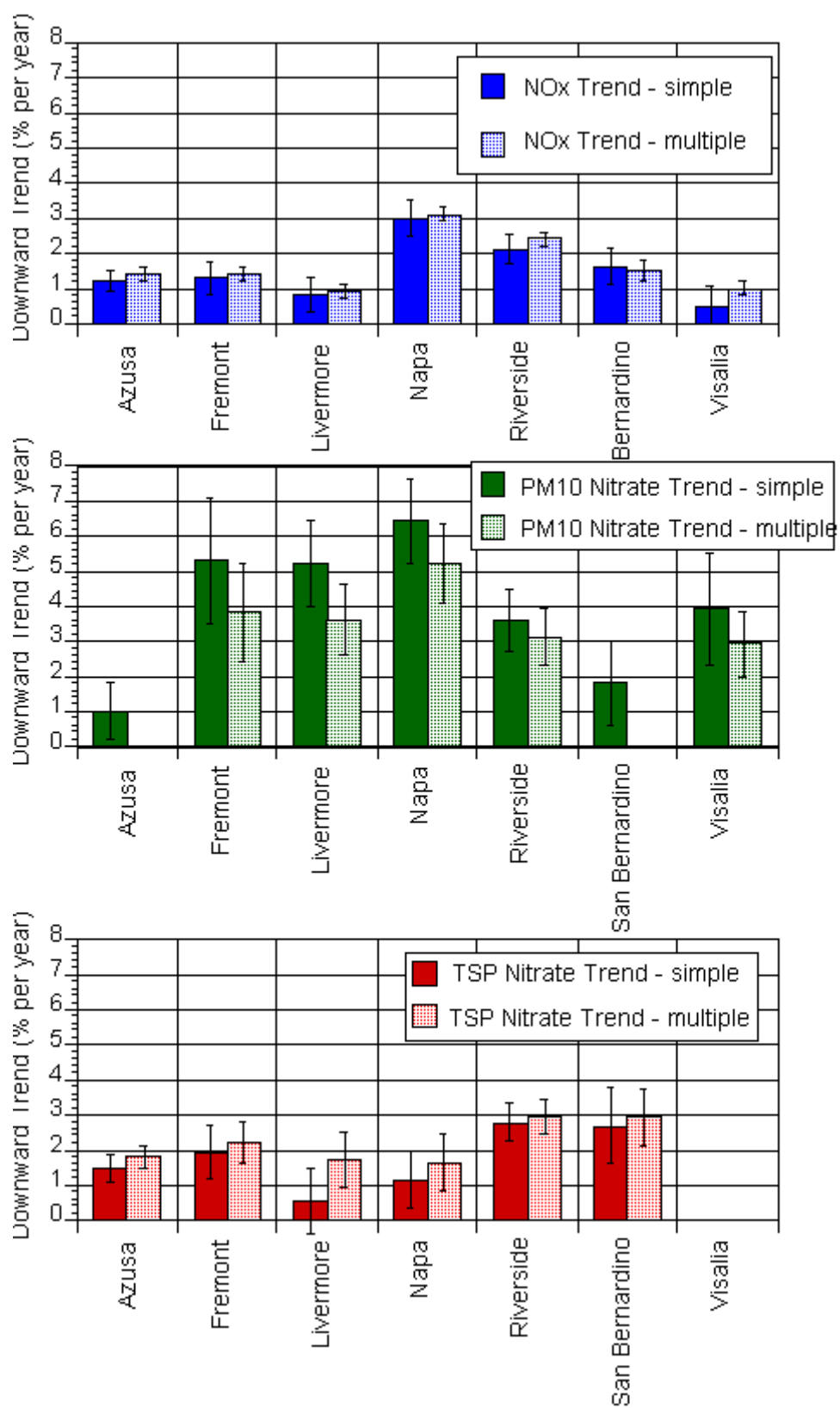


Figure 38. Comparison of downward trends determined from simple and multiple regressions. Error bars are one standard error. All sites had measurements from at least ten years within the period from 1980 through 1999.

The final column in Table 9 shows that inclusion of ambient NO_x , CO, and CoH concentrations in addition to temperature and precipitation explains the PM_{10} nitrate trends. That is, PM_{10} nitrate levels show no trend beyond that which is related to changes in ambient NO_x , CO, and CoH concentrations, temperature, and precipitation. Thus, nitrate levels have responded to primary pollutant changes. But because the magnitudes of the NO_x trends alone were insufficient to account for the nitrate trends, it is likely that ambient nitrate levels have responded to reductions of primary pollutants in addition to NO_x . However, it is difficult to determine which primary pollutant reductions have influenced PM nitrate levels. The regression coefficients link PM_{10} nitrate and TSP nitrate to NO_x , but also to CO or CoH at some sites (Figure 39). The measurements do not permit more exact determination of the specific effects of changes in each primary pollutant on ambient PM_{10} or TSP nitrate, because all pollutants generally exhibited the same pattern of accelerated decline during the 1990s (Figures 19-25 and 33-35).

In contrast, analyses of the weekend effect in southern California have shown that weekend NO_x levels are significantly lower than weekday levels, but no statistically significant differences exist between weekday and weekend levels of $\text{PM}_{2.5}$ nitrate, PM_{10} nitrate, or TSP nitrate (Blanchard and Tanenbaum, 2003). Compared with weekdays, weekends show a much stronger reduction of ambient NO_x levels than of ambient hydrocarbon concentrations (Chinkin et al., 2003). The weekend emission pattern thus differs from the historical record, which shows strong reductions of all primary pollutant levels. The absence of nitrate reductions on weekends in response to lowered NO_x levels at least suggests that the historical nitrate trends are related in part to reductions of primary pollutants in addition to NO_x .

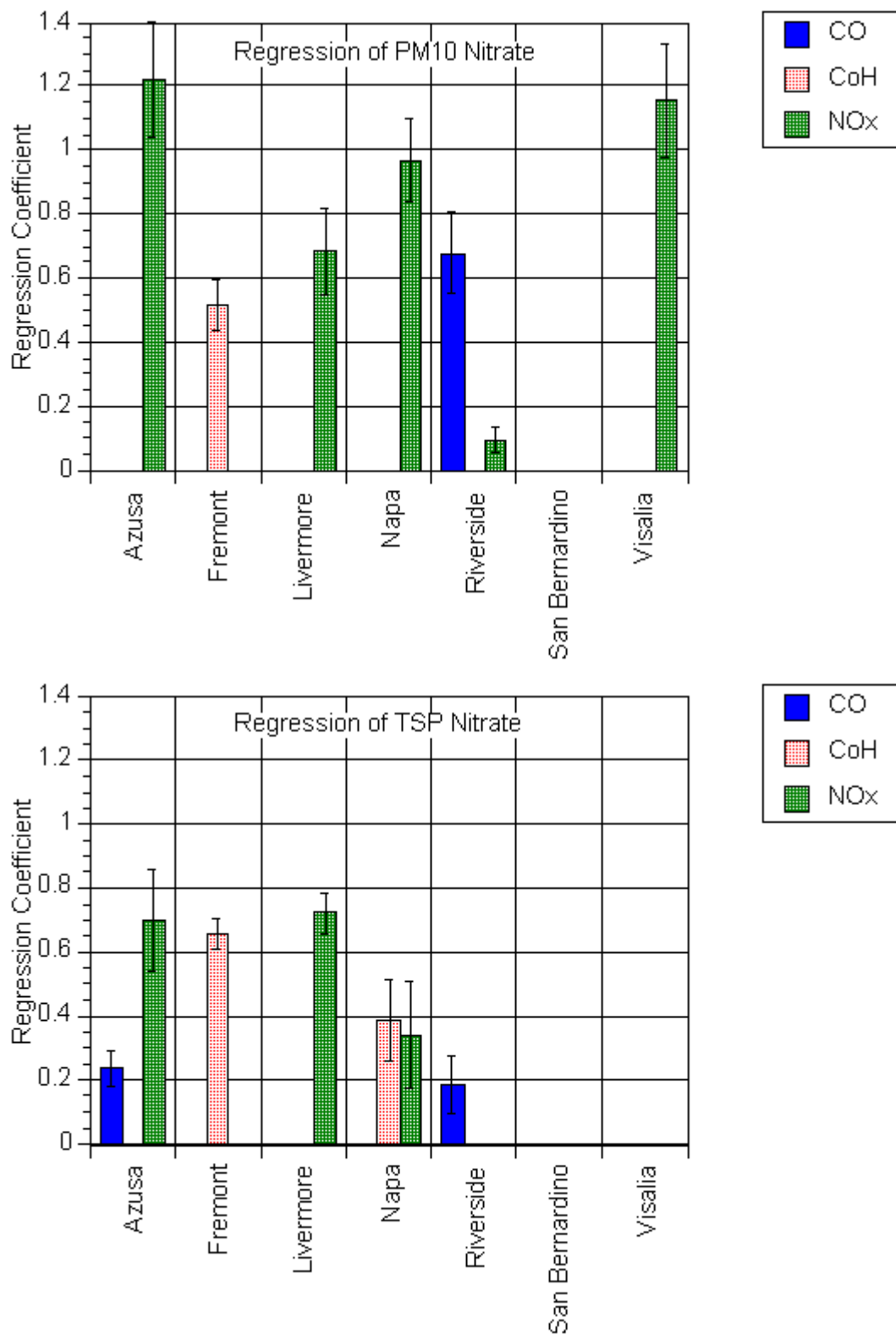


Figure 39. Regression coefficients relating PM₁₀ nitrate and TSP nitrate to primary pollutants (CO, CoH, and NO_x). Because of the use of logarithms, a coefficient of unity implies a linear and proportional mathematical form of the regression relationship. Error bars are one standard error. All sites had measurements for at least ten years from 1980 through 1999.

The complete regression results are listed in Tables 10 through 16. The tabled values include the R^2 , the number of months of data, and the regression coefficients for all statistically significant ($p < 0.05$) parameters. Because of the use of logarithms, the coefficient for time may be interpreted as fractional change per year (e.g., a coefficient -0.019 implies a fractional decrease of 0.019 per year, which is the same as a 1.9 percent per year decline). The coefficients associated with precipitation amount, NO_x , CO, and CoH indicate how a one unit change in each of these parameters would affect each of the dependent variables. Because logarithms were used for the species concentrations, a coefficient of, e.g., -0.05 for regression of PM_{10} mass against precipitation means that a one unit change in precipitation amount changes the log of PM_{10} mass by -0.05 units. A coefficient of 0.5 for the row labeled NO_x in the column labeled PM_{10} nitrate means that a change in NO_x yields a square root change in PM_{10} nitrate. The sine and cosine terms complete the statistical model in each case, but the values of their coefficients generally are not informative; these terms model the seasonal and multi-year periodicities, so that they are separated from the long-term trends and the relations among the pollutants.

Table 10. Regression coefficients for trends at Riverside. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.819	0.656	0.306	0.392	0.719	0.495	0.495
No. months	221	180	180	172	215	215	207
NO _x -cool	---	---	---	0.095	---	---	
NO _x -warm	---	---	---		---	---	
Precipitation	-0.04	-0.083	-0.111	-0.088	-0.077	-0.073	-0.079
Temperature	0.021	0.025			0.022	0.037	0.036
Time-cool	-0.02	-0.031	-0.031		-0.025	-0.029	-0.023
Time-warm	-0.02	-0.031	-0.031		-0.025	-0.029	-0.023
sin(2 π t/4)			0.117	0.152			
cos(2 π t/4)				-0.106			
sin(2 π t/5)							
cos(2 π t/5)	0.037						
sin(2 π t/6)							
cos(2 π t/6)							
sin month	-0.189			0.209	-0.058	0.102	0.131
cos month	0.725			-0.56			
CO	---	---	---	0.68	---	---	0.187
CoH	---	---	---	---	---	---	---

Table 11. Regression coefficients for trends at Azusa. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.61	0.626	0.195	0.27	0.74	0.587	0.599
No. months	245	178	178	175	233	233	228
NO _x -cool	---	---	---	1.223	---	---	0.699
NO _x -warm	---	---	---		---	---	0.323
Precipitation	-0.026	-0.047	-0.062		-0.056	-0.052	-0.028
Temperature	0.024	0.027			0.024	0.018	
Time-cool	-0.014	-0.033		-0.002	-0.023	-0.018	-0.001
Time-warm	-0.014	-0.033			-0.023	-0.018	
sin(2 π t/4)		-0.06					
cos(2 π t/4)		0.08			0.052		
sin(2 π t/5)	0.049						
cos(2 π t/5)					0.052		
sin(2 π t/6)	0.055						
cos(2 π t/6)	-0.091						
sin month	-0.103				-0.087		0.105
cos month	0.284				-0.219		-0.244
CO	---	---	---		---	---	0.235
COH	—	---	---	---	---	---	—

Table 12. Regression coefficients for trends at San Bernardino. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.731	0.635	0.166	0.169	0.749	0.45	0.45
No. months	170	159	159	154	161	161	156
NO _x -cool	---	---	---		---	---	
NO _x -warm	---	---	---		---	---	
Precipitation	-0.024	-0.056	-0.099	-0.099	-0.067	-0.051	-0.051
Temperature		0.027			0.029	0.029	0.03
Time-cool	-0.015	-0.037			-0.03	-0.029	-0.03
Time-warm	-0.015	-0.037			-0.03	-0.029	
sin(2 π t/4)			0.15	0.152			0.093
cos(2 π t/4)							
sin(2 π t/5)							
cos(2 π t/5)		0.059			0.066		
sin(2 π t/6)							
cos(2 π t/6)	-0.059				-0.06		
sin month	-0.223	-0.071			-0.085		
cos month	0.268	-0.365			-0.414		
CO	---	---	---		---	---	
CoH	---	---	---	---	---	---	—

Table 13. Regression coefficients for trends at Visalia. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.867	0.761	0.722	0.717	0.556	na	na
No. months	219	155	168	147	78	0	0
NO _x -cool	---	---	---	1.155	---	na	na
NO _x -warm	---	---	---	0.926	---	na	na
Precipitation	-0.084	-0.154	-0.305	-0.219	-0.204	na	na
Temperature			-0.038				
Time-cool	-0.01	-0.045	-0.029			na	na
Time-warm	-0.01	-0.045	-0.029			na	na
sin(2 π t/4)	-0.039		-0.114			na	na
cos(2 π t/4)		0.07	0.142			na	na
sin(2 π t/5)	0.065		0.166			na	na
cos(2 π t/5)		0.157				na	na
sin(2 π t/6)	0.105		0.179		0.117	na	na
cos(2 π t/6)	-0.043	0.115	-0.106			na	na
sin month	-0.303	-0.311	-0.138	0.216	-0.148	na	na
cos month	0.493		0.496			na	na
CO	---	---	---		---	---	0
CoH	—	---	---		---	---	na

Table 14. Regression coefficients for trends at Livermore. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.88	0.64	0.472	0.564	0.519	0.412	0.509
No. months	235	155	162	110	167	152	152
NO _x -cool	---	---	---	0.684	---	---	0.721
NO _x -warm	---	---	---	0.684	---	---	0.721
Precipitation	-0.056	-0.112	-0.202	-0.195	-0.107	-0.138	-0.094
Temperature			-0.051	-0.029			
Time-cool	-0.009	-0.042	-0.036		-0.028		
Time-warm	-0.009	-0.042	-0.036		-0.028		
sin(2 π t/4)	-0.009	0.079					
cos(2 π t/4)							
sin(2 π t/5)			0.118		-0.084		
cos(2 π t/5)		0.158					
sin(2 π t/6)						0.1	0.100
cos(2 π t/6)		0.184		0.161	0.117		
sin month	-0.281	-0.212	-0.193		-0.166	-0.188	
cos month	0.561	0.24			0.112		
CO	---	---	---		---	---	
CoH	---	---	---		---	—	

Table 15. Regression coefficients for trends at Fremont. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.89	0.566	0.467	0.532	0.505	0.42	0.533
No. months	248	128	128	128	137	184	183
NO _x -cool	---	---	---		---	---	
NO _x -warm	---	---	---		---	---	
Precipitation	-0.059	-0.123	-0.254	-0.218	-0.063	-0.134	-0.096
Temperature	0.017		-0.039	-0.036			
Time-cool	-0.014	-0.029	-0.038		-0.022	-0.022	-0.018
Time-warm	-0.014	-0.029	-0.038		-0.022	-0.022	-0.018
sin(2 π t/4)					0.062		
cos(2 π t/4)	-0.031						
sin(2 π t/5)					0.059		
cos(2 π t/5)							
sin(2 π t/6)							
cos(2 π t/6)						0.08	0.071
sin month	-0.287	-0.178			-0.159	-0.222	
cos month	0.702	0.295			0.138	0.4	
CO	---	---	---		---	---	
CoH	—	—	—	0.515	---	---	0.656

Table 16. Regression coefficients for trends at Napa. The dependent (predicted) variables are listed in the column headings. The predictor variables are listed in the column labeled “Parameter.” A cell with dashes (—) indicates that the predictor variable was not tried in the regression. A blank cell indicates that the predictor variable was tried but was not statistically significant ($p < 0.05$). A cell with a value indicates a statistically significant result. All measurements spanned at least ten years within the period from 1980 through 1999.

Parameter	NO _x	PM ₁₀	PM ₁₀ NO ₃		TSP	TSP NO ₃	
			w/o primary species	with primary species		w/o primary species	with primary species
R ²	0.933	0.758	0.362	0.425	0.55	0.425	0.474
No. months	229	157	163	159	152	152	151
NO _x -cool	---	---	---	0.968	---	---	0.487
NO _x -warm	---	---	---	0.968	---	---	0.594
Precipitation	-0.033	-0.041	-0.074	-0.045	-0.04	-0.039	
Temperature	-0.011	-0.034					0.025
Time-cool	-0.031	-0.052	-0.052		-0.02	-0.016	
Time-warm	-0.031	-0.052	-0.052		-19	-0.016	
sin(2 π t/4)							
cos(2 π t/4)							
sin(2 π t/5)		0.059	0.177	0.166			
cos(2 π t/5)							
sin(2 π t/6)							
cos(2 π t/6)							
sin month	-0.306	-0.285	-0.141		-0.187	-0.275	
cos month	0.604		0.431		0.231	0.379	
CO	---	---	---		---	---	
CoH	---	---	---		---	---	0.386

In summary, the multiple regressions show that:

- All compound concentrations were related to variations in precipitation.
- NO_x levels were inversely related to precipitation amount and declined over time at all 7 sites.
- PM_{10} and TSP mass were inversely related to precipitation amount at all 7 sites. PM_{10} mass declined over time at all 7 sites and TSP mass declined over time at 6 sites.
- PM_{10} nitrate concentrations were inversely related to precipitation amount at 6 sites, declined over time at 5 sites, and were positively related to NO_x levels at 5 sites.
- TSP nitrate concentrations were inversely related to precipitation amount at 6 sites, declined over time at 4 sites, and were positively related to NO_x levels at 5 sites.
- When NO_x , CO, and CoH were included in the regressions as predictor variables, the time trends in PM_{10} nitrate and TSP nitrate concentrations disappeared (i.e., the time trends in PM_{10} nitrate and TSP nitrate were described by the time trends in NO_x , CO, and CoH).

CONCLUSION

From 1980 to 2000, ambient PM_{10} nitrate concentrations decreased at faster rates than did ambient NO_x concentrations at the majority of California monitoring locations studied. At monitoring sites in the South Coast, South Central Coast, and Mojave Desert air basins, the mean rate of decline of monthly-average PM_{10} nitrate concentrations was 0.304 percent per month (mean S.E. 0.109 percent per month), whereas the mean rate of decline of monthly-average NO_x was 0.080 percent per month (mean S.E. 0.080 percent per month). The ambient NO_x declines tended to be greater near the coast, whereas the PM_{10} nitrate declines tended to be greater in the northern South Coast Air Basin and north of the basin. Of 16 southern California sites with both NO_x and PM_{10} measurements, five showed opposite trends in NO_x and PM_{10} nitrate concentrations (two had increasing PM_{10} nitrate with decreasing NO_x , while three had decreasing PM_{10} nitrate with increasing NO_x). Six sites showed trends in PM_{10} nitrate and NO_x that were directionally the same but differed in magnitude by factors of two to four (4 sites with greater trends in PM_{10} nitrate than in NO_x). Five sites (Anaheim, Azusa, Burbank, San Bernardino, and Santa Clarita) showed quantitatively similar trends for NO_x and PM_{10} nitrate. Decreasing trends were evident for all compounds studied at the majority of monitoring sites in the South Coast, South Central Coast, and Mojave Desert air basins: PM_{10} mass (50 of 53 sites declined, with 37 declines statistically significant), NO_x (34 of 48 sites declined, with 25 declines statistically significant), PM_{10} nitrate (20 of 25 sites declined, with 12 declines statistically significant), and TSP nitrate (25 of 38 sites declined, with 13 declines statistically significant).

At the seven long-term monitoring sites whose data were studied in more detail, the trends in PM_{10} nitrate also exceeded trends in NO_x : as determined from simple regressions of concentration against time, the median NO_x trend at these seven sites was a decline of 1.3 percent per year, whereas the median PM_{10} nitrate trend was a decline of 3.6 percent per year. As determined from stepwise multiple regressions that included the effects of temperature and precipitation, the median NO_x trend was a decline of 1.4 percent per year, whereas the median PM_{10} nitrate trend was a decline of 3.1 percent per year. These differences indicate that declining NO_x levels alone were not responsible for declining nitrate concentrations, because PM_{10} nitrate is not expected to exhibit a greater than proportional response to changing NO_x levels.

The stepwise multiple regressions confirmed the trends estimated from the simple regressions. The median trends in NO_x , 1.3 percent per year for the simple regressions and 1.4 percent per year for the multiple regressions, agreed closely. For PM_{10} mass, the median trend was 3.3 percent per year for the simple regressions and 3.7 percent per year for the multiple regressions. For PM_{10} nitrate, the median trend was a decline of 3.6 percent per year for the simple regressions and 3.1 percent per year for the stepwise multiple regressions. The trends in NO_x , PM_{10} mass, TSP mass, PM_{10} nitrate, and TSP nitrate occurred during both warm and cool seasons.

Monthly average concentrations of NO_x , PM_{10} mass, TSP mass, PM_{10} nitrate, and TSP nitrate all varied inversely with precipitation amount. NO_x , PM_{10} mass, and TSP mass varied directly with temperature at 4 of the 7 sites. When PM_{10} nitrate and TSP nitrate varied with temperature, the relationship was inverse for PM_{10} nitrate but direct for TSP nitrate. Temperature and precipitation trends contributed to the trends in PM_{10} nitrate and TSP nitrate.

Inclusion of ambient NO_x , CO, and CoH concentrations in addition to temperature and precipitation in the statistical models accounted for the PM_{10} nitrate trends, since PM_{10} nitrate levels showed no trend beyond that which was related to changes in ambient NO_x , CO, and CoH concentrations, temperature, and precipitation. Thus, nitrate levels have responded to primary pollutant changes. But because the magnitudes of the NO_x trends alone were insufficient to account for the nitrate trends, it is likely that ambient nitrate levels have responded to reductions of primary pollutants in addition to NO_x . The regressions linked PM_{10} nitrate and TSP nitrate to NO_x , but also to CO or CoH at some sites. The measurements do not permit more specific determination of the effects of each primary pollutant on ambient PM_{10} nitrate or TSP nitrate.

In comparison, analyses of the weekend effect in southern California have shown that weekend NO_x levels are significantly lower than weekday levels, but no statistically significant differences exist between weekday and weekend levels of $\text{PM}_{2.5}$ nitrate, PM_{10} nitrate, or TSP nitrate (Blanchard and Tanenbaum, 2003). Compared with weekdays, weekends show a much stronger reduction of ambient NO_x levels than of ambient hydrocarbon concentrations. The weekend emission pattern thus differs from the historical record, which shows strong reductions

of all primary pollutant levels. The absence of nitrate reductions on weekends in response to lowered NO_x levels suggests that the historical nitrate trends are related in part to reductions of primary pollutants in addition to NO_x .

Primary PM_{10} mass was estimated as: primary mass = mass-sulfate- nitrate- ammonium. At the seven long-term sites, the estimated primary TSP mass declined by 1.9 to 3.0 percent per year, and the estimated primary PM_{10} mass declined by 2.4 to 4.8 percent per year. In contrast, inventory primary PM_{10} emissions show no decline. This discrepancy warrants further analysis.

The present study does not evaluate the consistency of trends in estimated primary pollutant emissions and ambient concentrations at the full set of monitors in any of California's air basins. Measurement biases associated with the available monitoring data also limit the reliability of the trend assessments. Additional efforts, including application of this study's statistical and graphical techniques to more locations, are needed to further clarify how PM_{10} nitrate and $\text{PM}_{2.5}$ nitrate levels have responded to emission changes throughout California.

GLOSSARY

CADMP	California Acid Deposition Monitoring Program
CHS TWS	Children's Health Study Two-Week Sampler
CO	carbon monoxide
CoH	coefficient of haze
HNO ₃	nitric acid
IMPROVE	Interagency Monitoring of Protected Visual Environments
IMS95	Integrated Monitoring Study, 1995
ln	natural logarithm
μg m ⁻³	micrograms per cubic meter
NMHC	nonmethane hydrocarbons
NO _x	oxides of nitrogen
PM	particulate matter
PM ₁₀	particulate matter less than 10 μmeter aerodynamic diameter
ppbv	parts per billion by volume
PTEP	PM ₁₀ Enhancement Program
SCAPE2	Simulating Composition of Atmospheric Particles at Equilibrium, version 2
SCAQS	Southern California Air Quality Study
SoCAB	South Coast Air Basin
SSI	Size-selective inlet
TSP	total suspended particulate

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