5. RELATIONS BETWEEN PARTICULATE NITRATE AND OTHER SPECIES

In this section, we describe relations between ambient concentrations of particulate nitrate and other species. We also attempt to relate the results to the earlier discussion of chemical reactions leading to particulate nitrate formation (Section 2).

PM nitrate concentrations tend to be lower at coastal sites and higher inland (Figures 43 and 44). These figures depict cool/wet-season averages for 1995-99, and, because so much variation exists in individual measurements, averages constructed over different time periods may vary from the values shown. Generally, Riverside shows higher nitrate levels than do other sites. As noted in the previous section, over the whole period of record, mean PM_{10} concentrations are lower on weekends than on weekdays at all but one site, while TSP nitrate levels are higher on weekends than on weekdays at about two-thirds of the sites. None of the weekday-weekend nitrate differences are statistically significant, however.

At individual monitoring sites, the mean seasonal ozone concentrations tend to vary with the ratio of NO_2/NO_x (Figures 47 to 51). The ratio of NO_2/NO_x roughly indicates photochemical aging: it is closer to zero when NO concentrations are substantially greater than NO_2 levels and approaches one when NO concentrations are much lower than NO_2 levels (the routine measurements include PAN, HNO_3, and possibly other NO_2 reaction products in the reported values of NO_2). Weekend levels of ozone and ratios of NO_2/NO_x are typically greater than weekday values, indicating that photochemical production rates tend to be greater on weekends than on weekdays. In contrast, nitrate levels do not vary systematically in relation to NO_2/NO_x levels, indicating that particulate nitrate formation rates are not very responsive to changes in the proportion of NO converted to NO_2 or PAN.

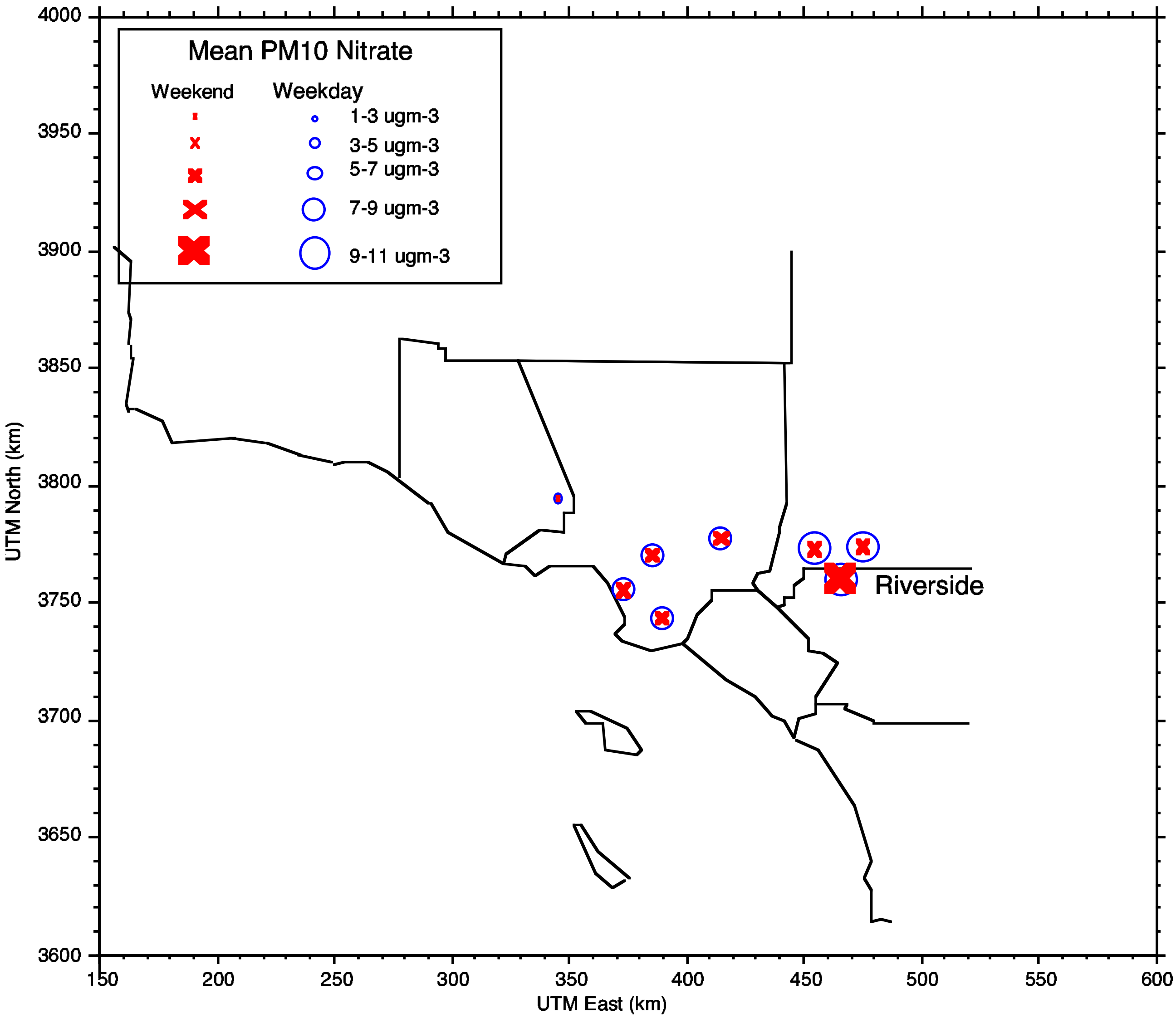


Figure 45. Mean weekend and weekday PM_{10} nitrate concentrations averaged over 1995-1999 at sites in the South Coast, South Central Coast, and Mojave Desert air basins. Each site average includes at least 30 daily measurements for weekends and 75 measurements for weekdays.

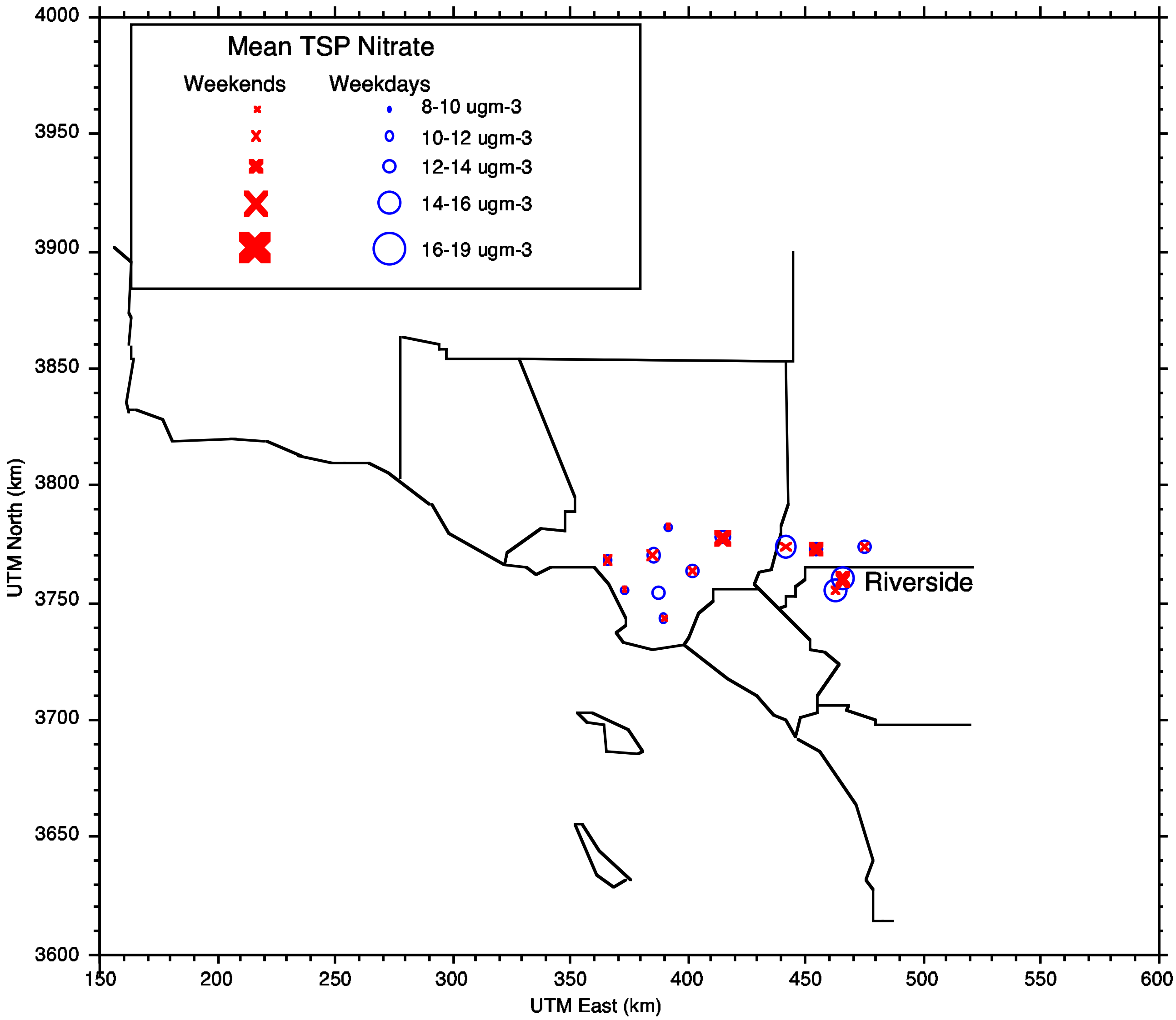


Figure 46. Mean weekend and weekday TSP NO_3 concentrations averaged over 1995-1999 at sites in the South Coast, South Central Coast, and Mojave Desert air basins. Each site average includes at least 30 daily measurements for weekends and 75 measurements for weekdays.

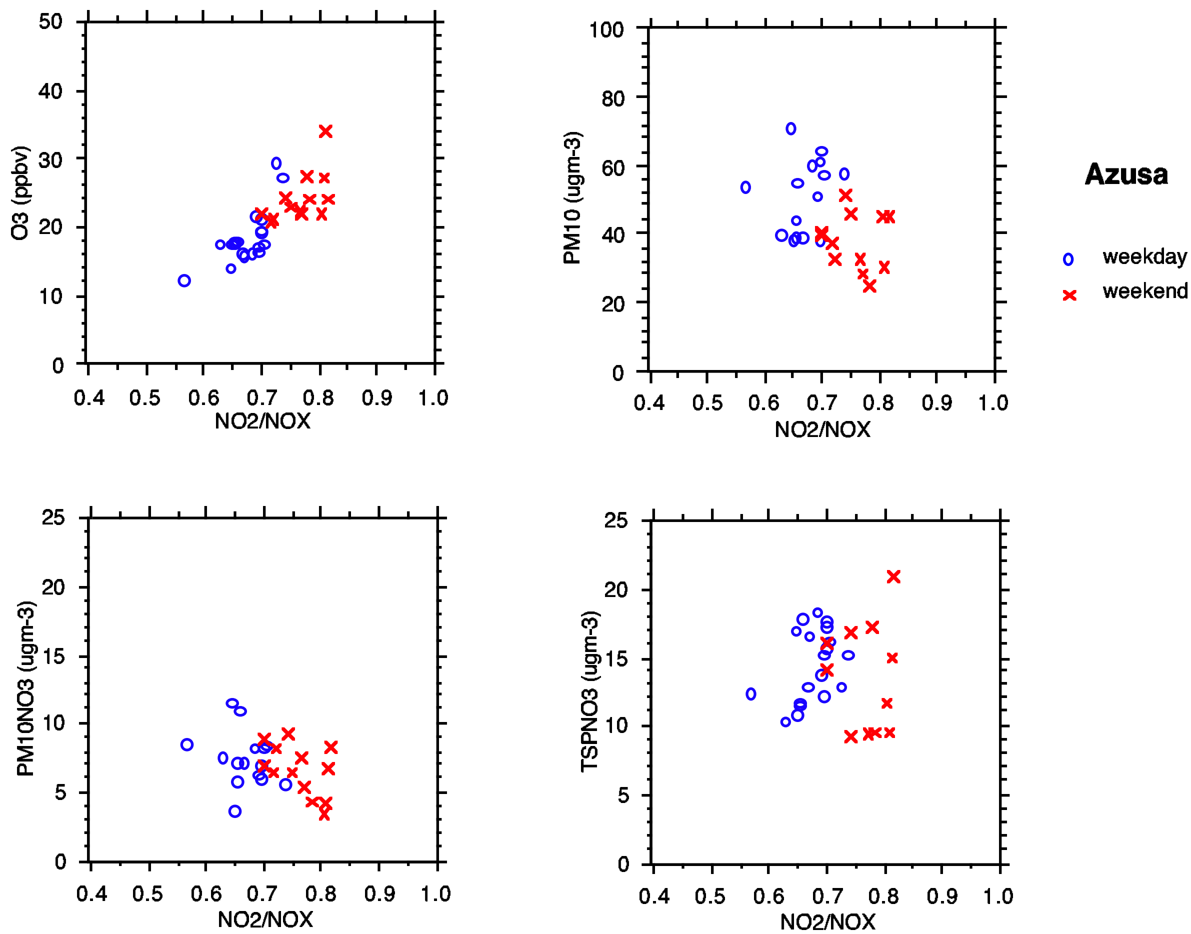


Figure 47. Mean seasonal concentrations of ozone, PM_{10}, PM_{10} NO_3, and TSP NO_3 compared to the ratio of mean NO_2 to mean NO_x at Azusa, 1980-1999. Each point is the average of 24-hour resolution samples collected on all days of PM sampling during the cool/wet or warm/dry season of one year (~25-30 samples per average).

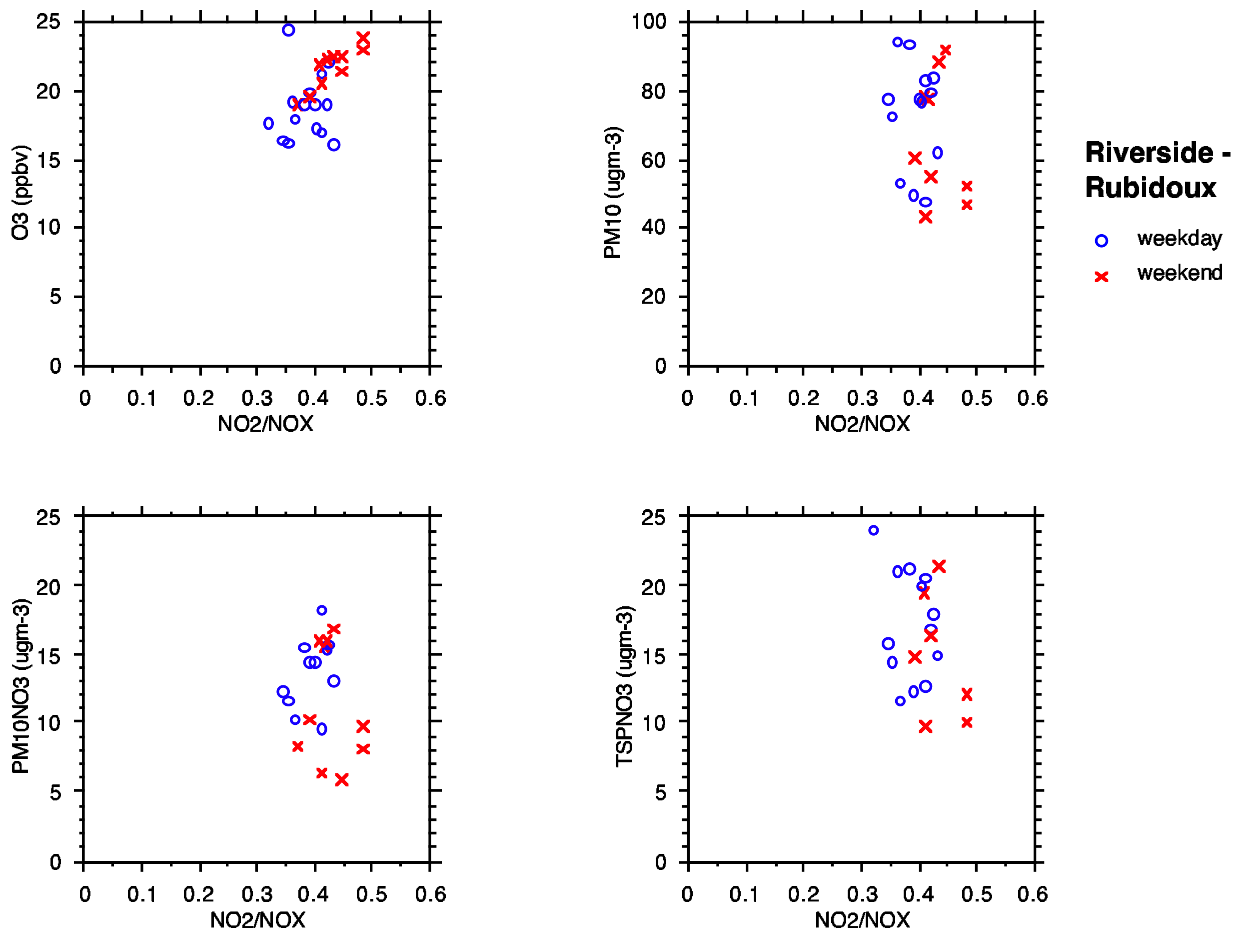


Figure 48. Mean seasonal concentrations of ozone, PM_{10}, PM_{10} NO_3, and TSP NO_3 compared to the ratio of mean NO_2 to mean NO_x at Riverside-Rubidoux, 1980-1999. Each point is the average of 24-hour resolution samples collected on all days of PM sampling during the cool/wet or warm/dry season of one year (~25-30 samples per average).

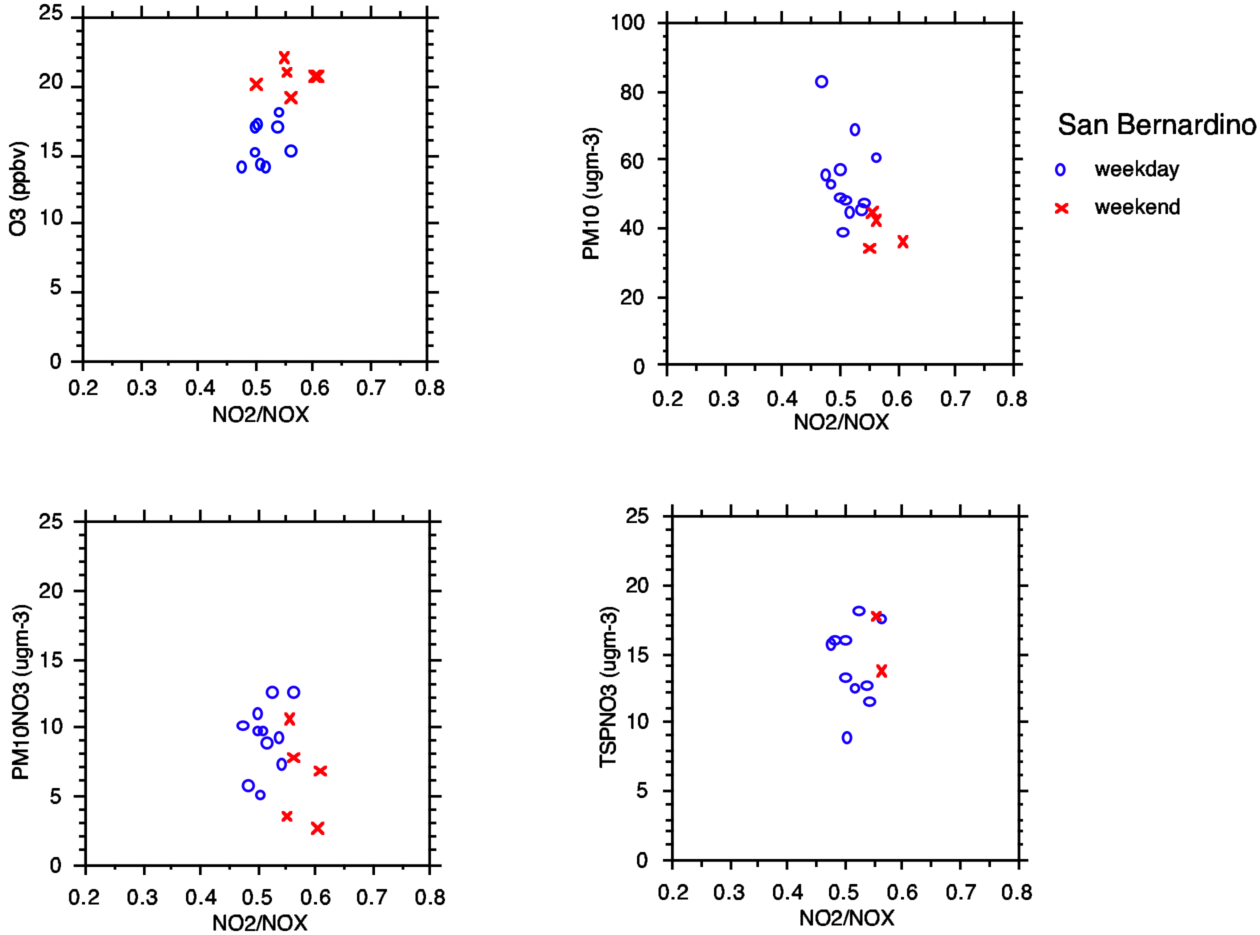


Figure 49. Mean seasonal concentrations of ozone, PM_{10}, PM_{10} NO_3, and TSP NO_3 compared to the ratio of mean NO_2 to mean NO_x at San Bernardino, 1980-1999. Each point is the average of 24-hour resolution samples collected on all days of PM sampling during the cool/wet or warm/dry season of one year (~25-30 samples per average).

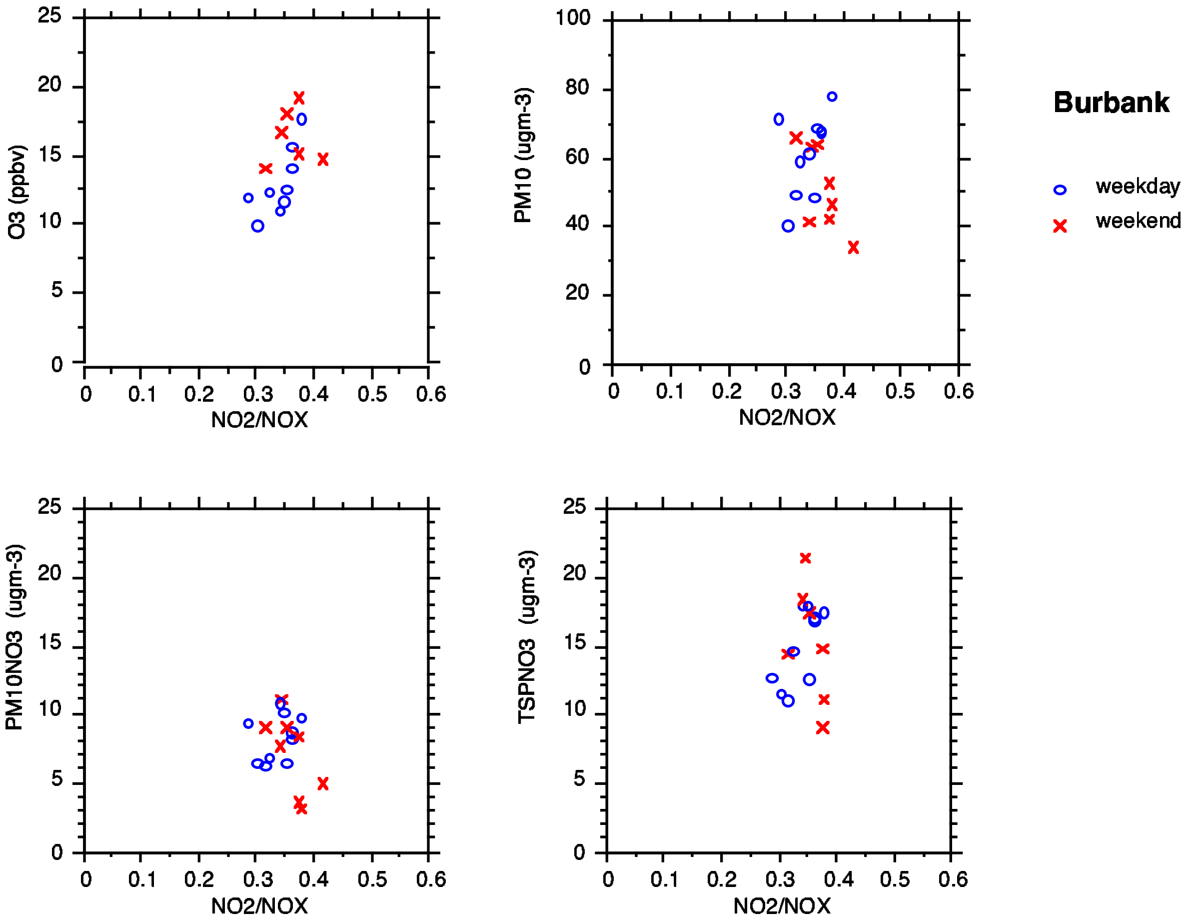


Figure 50. Mean seasonal concentrations of ozone, PM_{10}, PM_{10} NO_3, and TSP NO_3 compared to the ratio of mean NO_2 to mean NO_x at Burbank, 1980-1999. Each point is the average of 24-hour resolution samples collected on all days of PM sampling during the cool/wet or warm/dry season of one year (~25-30 samples per average).

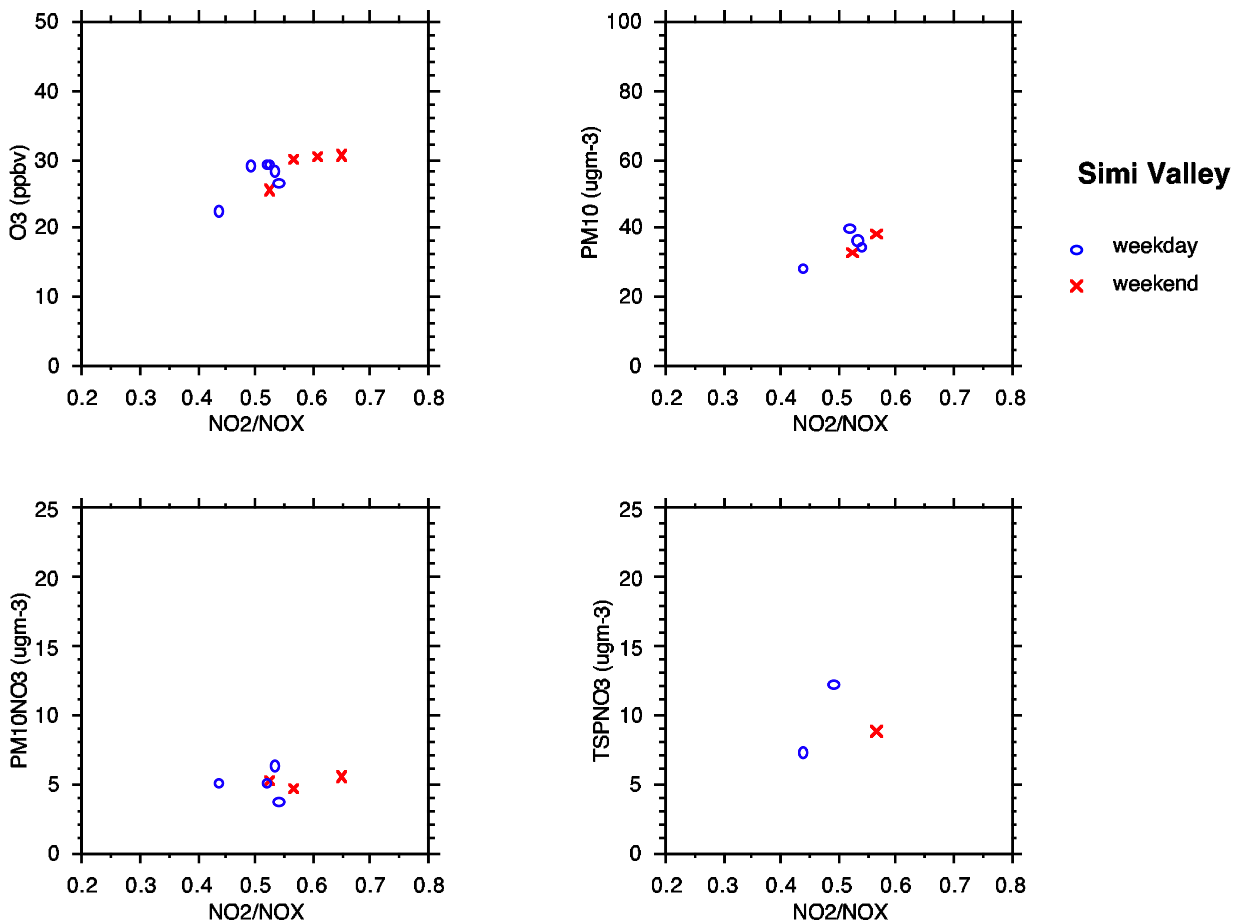


Figure 51. Mean seasonal concentrations of ozone, PM_{10}, PM_{10} NO_3, and TSP NO_3 compared to the ratio of mean NO_2 to mean NO_x at Simi Valley, 1980-1999. Each point is the average of 24-hour resolution samples collected on all days of PM sampling during the cool/wet or warm/dry season of one year (~25-30 samples per average).

Relation of Nitrate Levels to VOC/NO_x and CO/NO_x Ratios

We also attempted to relate the response - or lack of response - of weekend nitrate levels to changes in VOC/NO_x ratios on weekends. As shown in Section 4, weekends are characterized by lower CO, PM mass, and NO_x levels, statistically significant at most sites (Figure 28-29), during both cool/wet and warm/dry seasons. In the SoCAB, NMOC data are available from up to five locations for one or more years during the period 1994 to 1999. Canister samples were collected as three- hour averages every third or sixth day, during the months of June through September, so these measurements are limited in number and not available during the months when nitrate concentrations are usually the highest. These measurements show that lower NMOC concentrations occur on weekends, but the differences are not statistically significant (Table 3, Section 4). Two of the three sites having both NMOC and NO_x measurements show higher mean $NMOC/NO_x$ ratios on weekends. However, none of these differences of ratios are statistically significant. The highest summer nitrate levels are not associated with the highest VOC or NO_x levels (Figure 52). Instead, the highest summer nitrate levels are associated with more moderate levels of NMOC and NO_x, at an $NMOC/NO_x$ ratio of about 6:1, and occur on weekdays (Figure 50). The majority of the $NMOC/NO_x$ ratios were in the range of 4:1 to 6:1.

Carbon monoxide measurements are sometimes used as a surrogate for NMOC, because NMOC measurements are so limited. As shown in Figure 53, there were positive correlations between 24-hour average concentrations of CO and total NMOC at four sites having both measurements. However, considerable variability exists at each site, and the regression slopes varied among sites. Thus, ratios of CO/NO_x will not be used here as direct surrogates for $NMOC/NO_x$. Instead, the variation of nitrate with respect to the combined variation of CO and NO_x will be used in a more qualitative way to evaluate the possible dependencies of nitrate on precursor levels.

At Azusa, the highest PM nitrate and total nitrate (PM nitrate plus HNO_3) concentrations were associated with the highest levels of CO and NO_x (Figure 54). These higher ambient levels typically occurred during late autumn or winter. Since the correlation of CO and NO_x was so high, possible variations of nitrate with varying levels of CO/NO_x ratios are essentially unobservable.

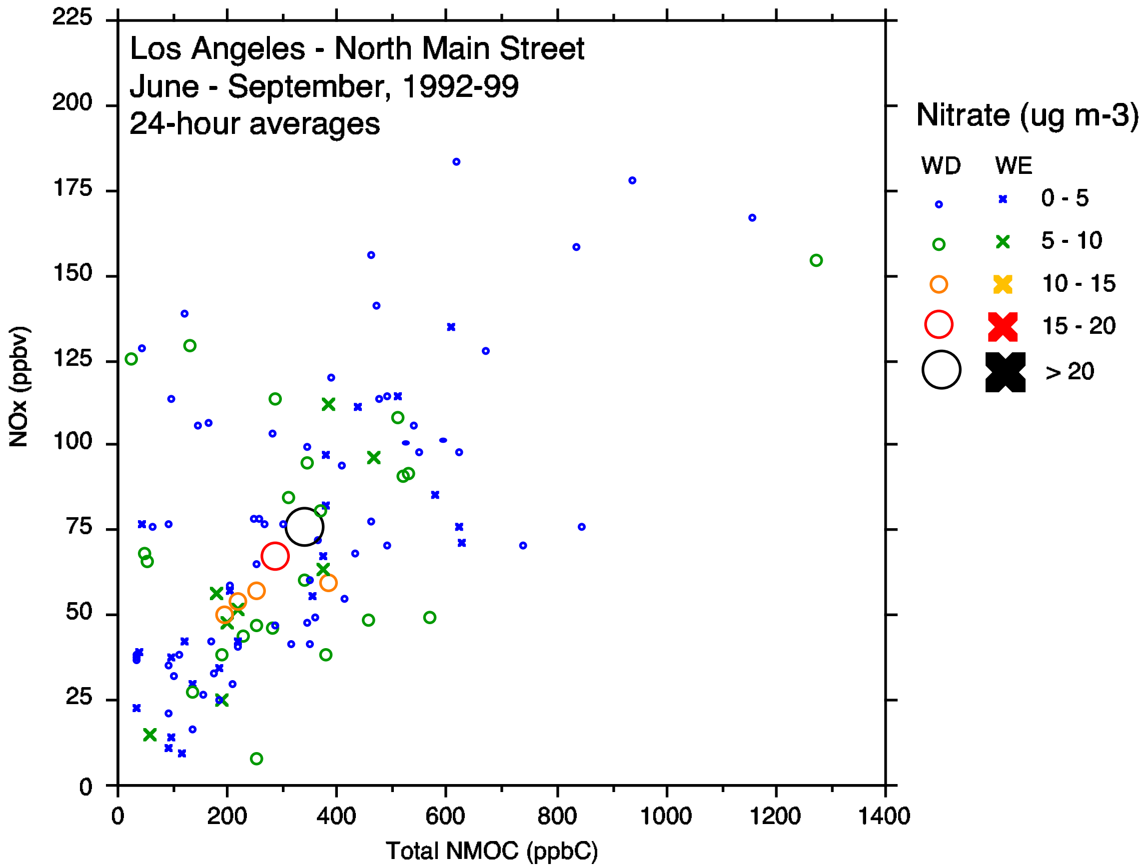


Figure 52. PM_{10} nitrate concentration versus NO_x and total NMOC at Los Angeles-North Main Street, 1992-99. All measurements were compiled as 24-hour averages and paired with PM_{10} nitrate concentrations on the PM sampling schedule. NMOC data were collected from June through September each year.

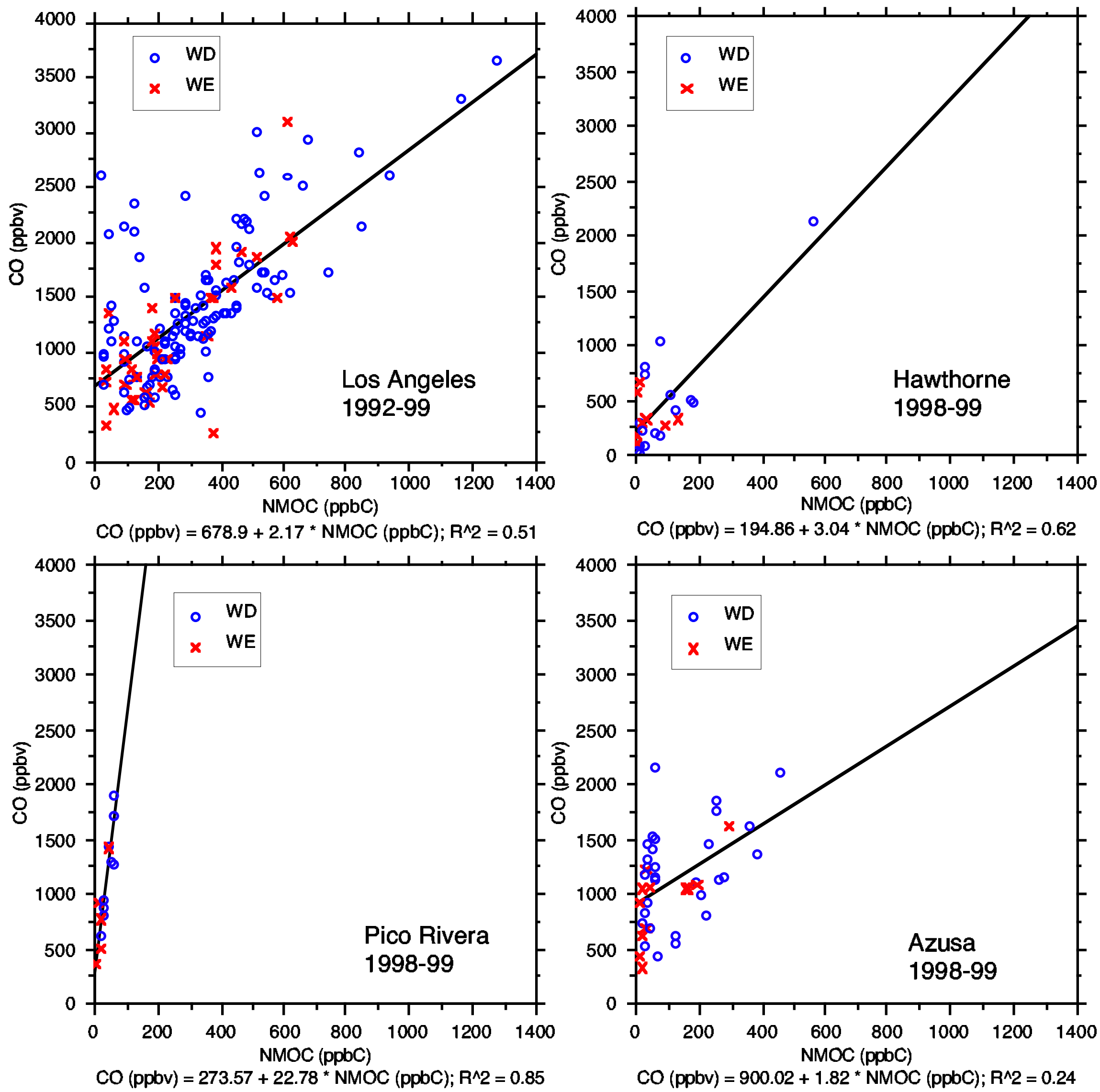
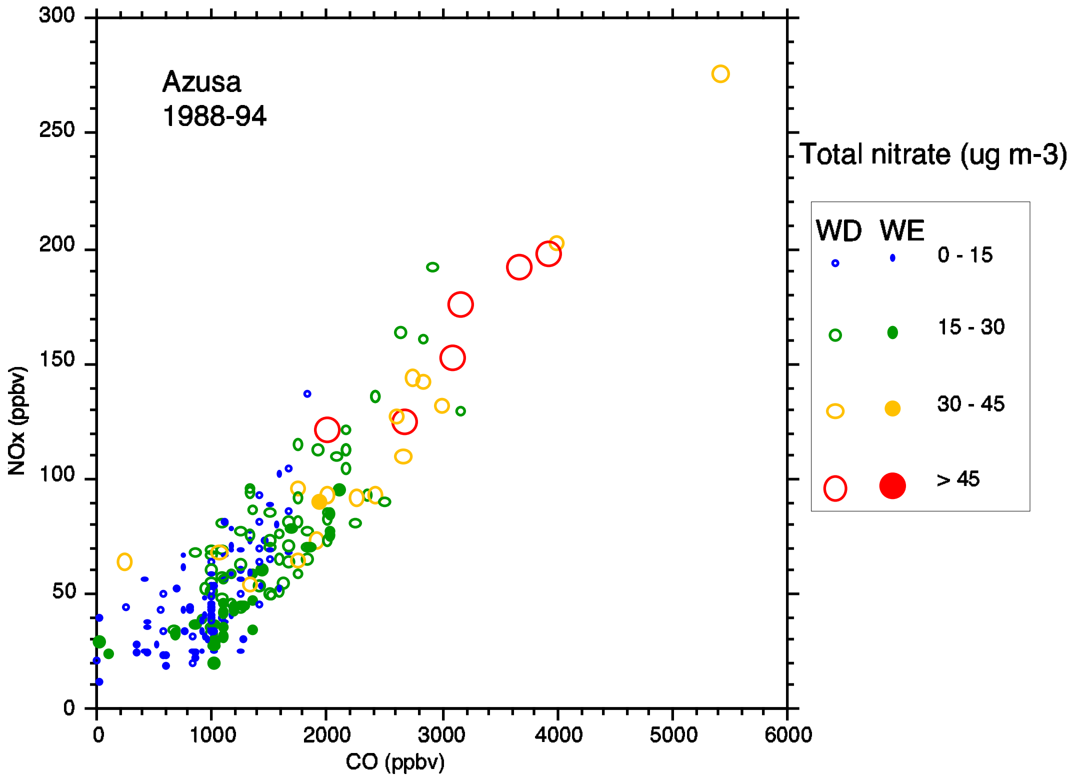


Figure 53. Comparison of 24-hour average CO to total NMOC concentrations at four sites.



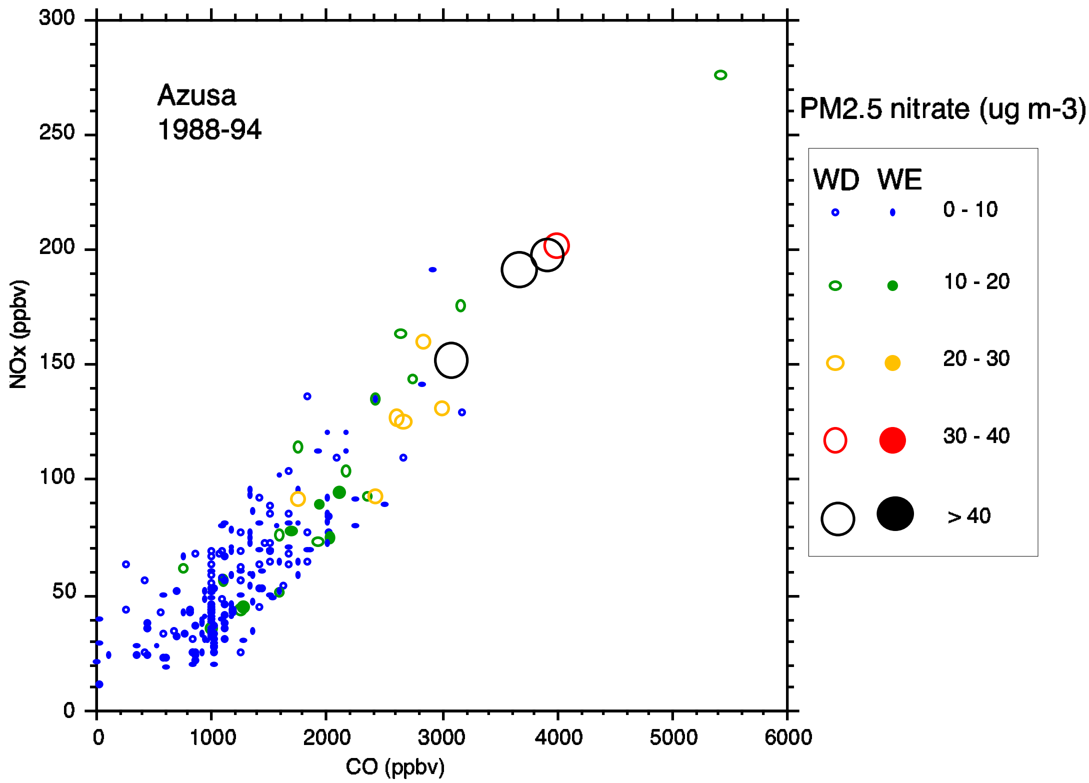


Figure 54. Daytime total nitrate (HNO_3 + particulate nitrate) and $PM_{2.5}$ nitrate versus CO and NO_x. All measurements represent 12-hour (6 am to 6 pm) averages.

Trends

At most sites, average nitrate levels are a small fraction of the mean NO_x concentrations (Fujita et al., 1992), as shown in Figures 53 and 54. In these plots, both NO_x and nitrate are shown in units of ppbv, with nitrate multiplied by ten to allow it to be visible on the plots. Thus, ambient NO_x concentrations provide an extensive reservoir for nitrate, so that nitrate is not limited by the availability of its precursor, NO_2. As discussed in Section 2, the conversion of NO_2 to HNO_3 may be radical limited rather than NO_x limited under some circumstances, and these comparisons of nitrate to NO_x levels suggest that the availability of NO_x is not limiting. If so, particulate nitrate levels typically would not be expected to show much responsiveness to changes in NO_x concentrations.

Some changes in particulate nitrate levels have occurred over time (Figures 57 and 58). Specifically, nitrate levels at some sites were somewhat lower during the period 1995-1999 than during earlier years. However, the differences over time are generally less than the magnitudes of the seasonal variations.

Trends were examined more systematically using linear regressions of log-transformed mean concentrations against time. For these regressions, monthly species average were first determined. Then, each monthly average was seasonally adjusted, as shown for the following example:

Adjusted average PM_{10} mass June 1995 =

PM_{10} mass June 1995/Mean of all June PM_{10} monthly mass averages

Finally, the logarithm of the preceding ratios was determined. These logarithms were then used as the dependent variables in a linear regression against time sequence (months, counting from the first month in the data record).

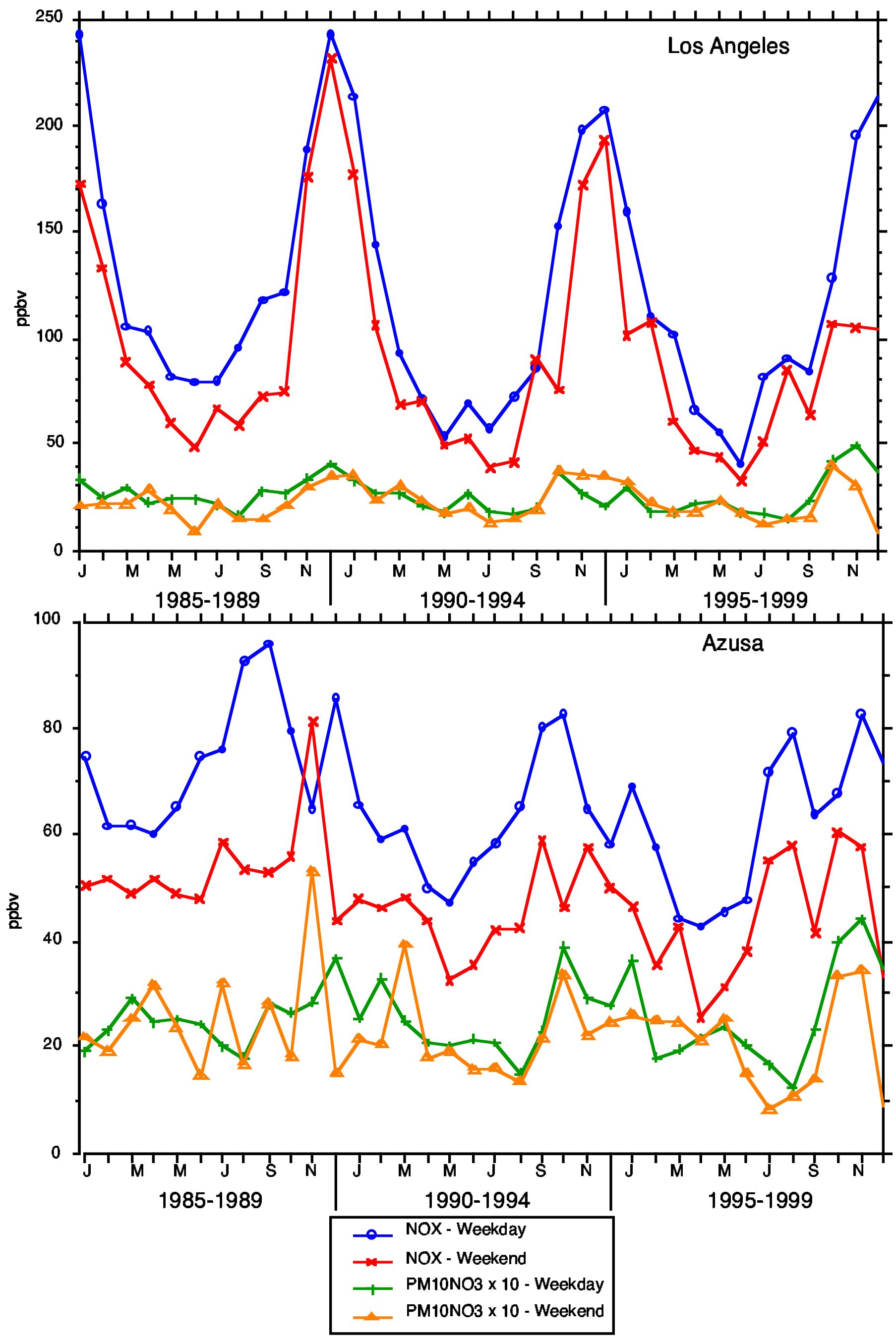


Figure 55. Monthly weekday and weekend averages of NO_x and PM_{10} nitrate at Los Angeles and Azusa during three time periods. Units of measurement are ppbv, and nitrate concentrations were multiplied by ten.

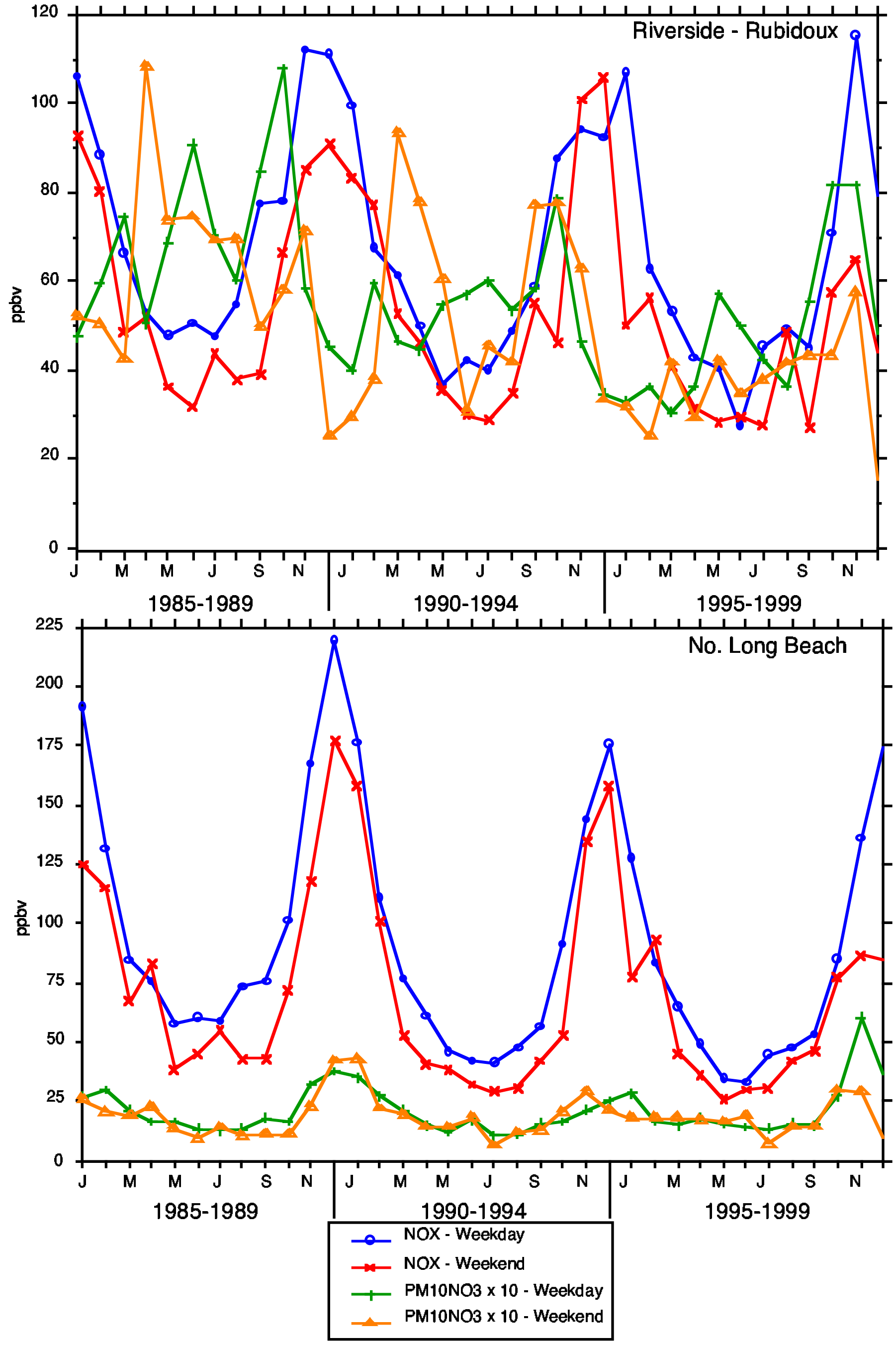


Figure 56. Monthly weekday and weekend averages of NO_x and PM_{10} nitrate at Riverside (Rubidoux) and North Long Beach during three time periods. Units of measurement are ppbv, and nitrate concentrations were multiplied by ten.

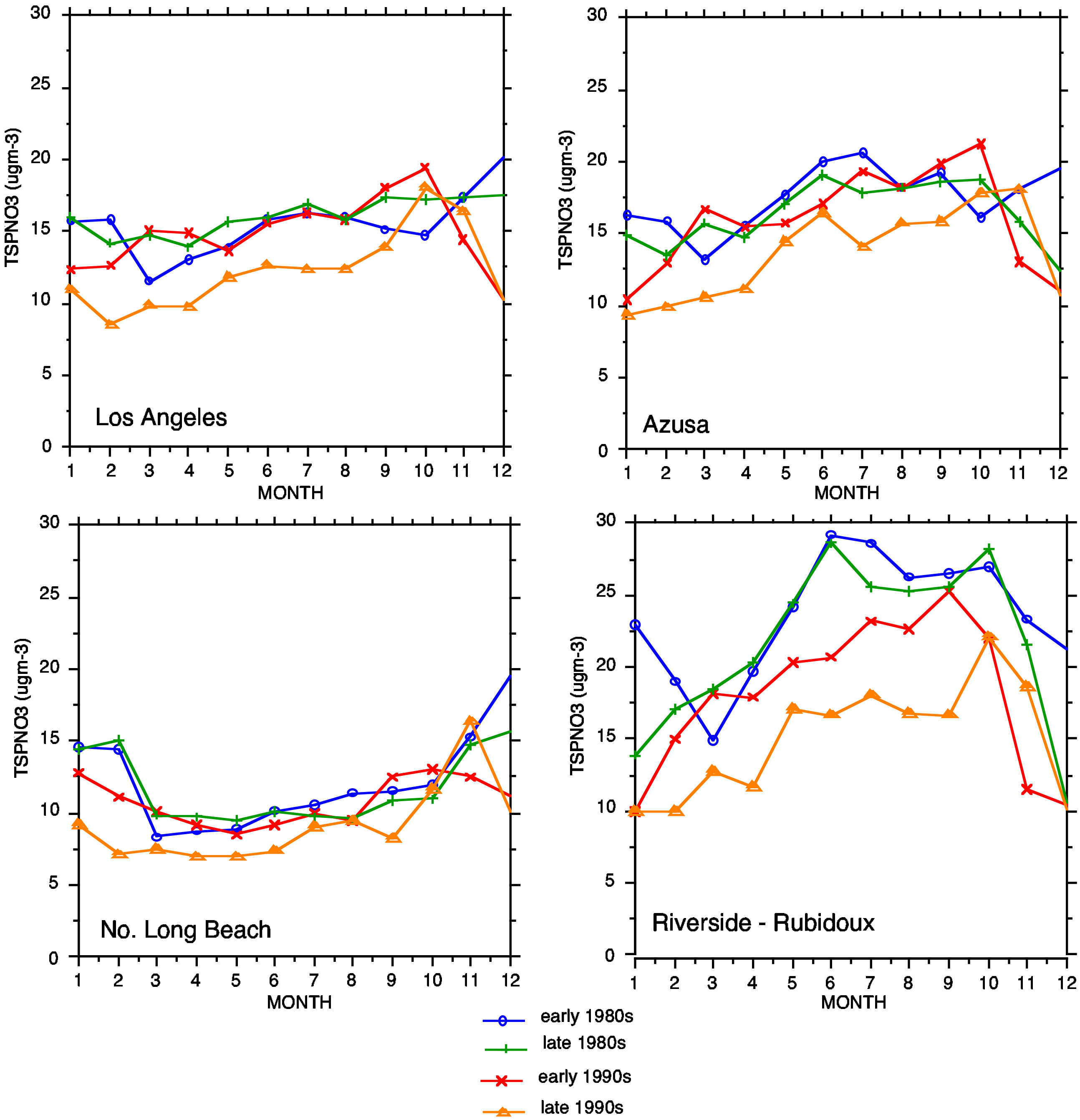


Figure 57. Monthly averages of TSP nitrate, computed from measurements within five-year periods: 1980-1984, 1985-89, 1990-94, and 1995-99.

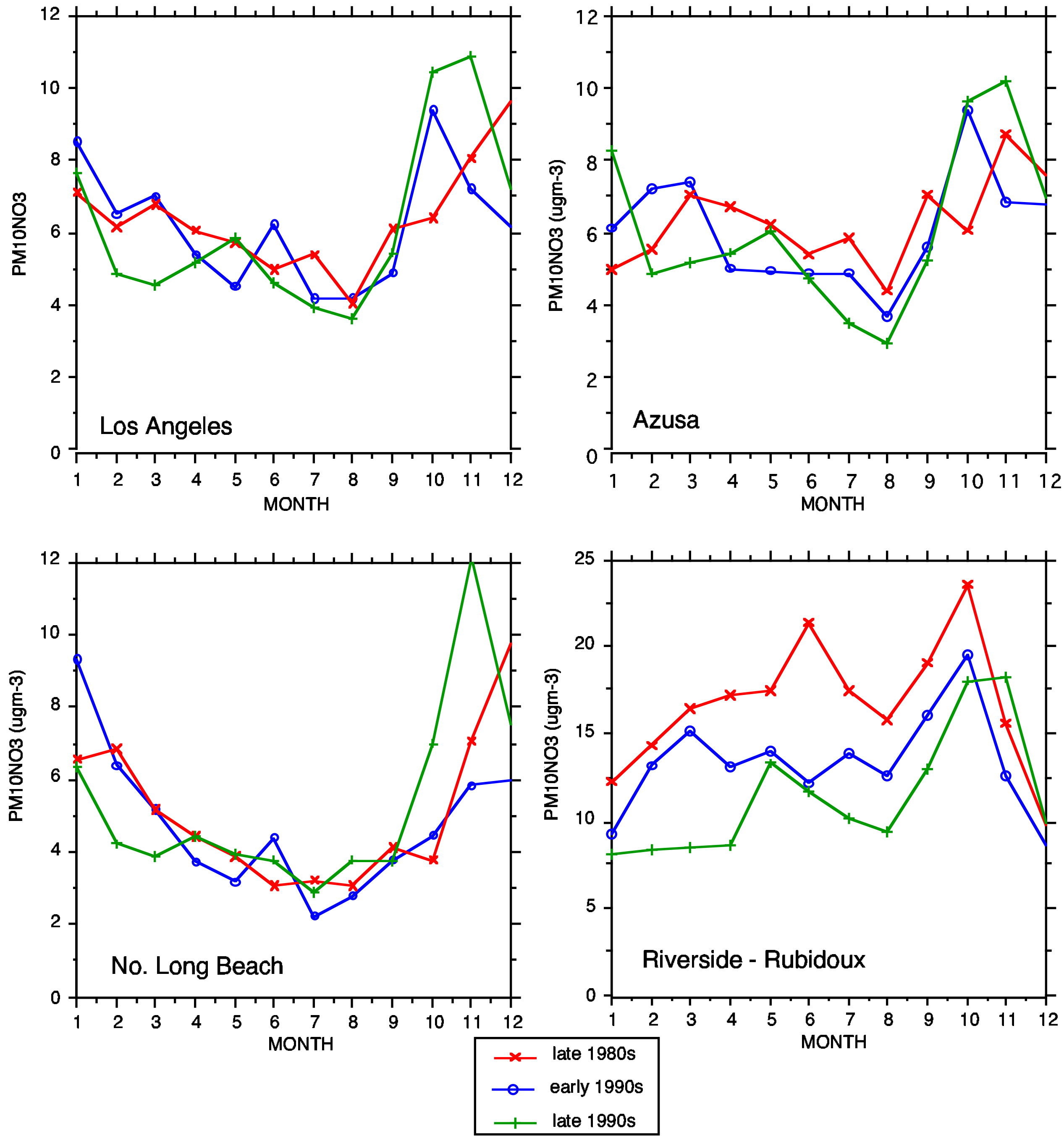


Figure 58. Monthly averages of PM_{10} nitrate, computed from measurements within five-year periods: 1980-1984, 1985-89, 1990-94, and 1995-99.

The regression results are shown for each site and each species, or ratio of species, in Tables 4 through 9. A summary of the numbers of sites with increasing or decreasing trends is shown in Table 10:

- PM_{10} mass declined at 50 of 53 sites, and 37 of the 50 declines were statistically significant.
- Monthly-average NO_x levels declined at 34 sites, but increased at 14 sites; 25 of the 34 decreases and 5 of the 14 increases were statistically significant (Table 10).
- PM_{10} nitrate declined at 20 sites and increased at 5 sites; 12 of the 20 declines were statistically significant.
- TSP nitrate declined at 25 sites and increased at 13 sites; 13 of the 25 declines and 1 of the 13 increases were statistically significant.
- The ratios of PM_{10} nitrate to NO_x decreased at 9 sites and increased at 6 sites; 5 of the 9 decreases and 2 of the 6 increases were statistically significant.
- The ratios of TSP nitrate to NO_x decreased at 9 sites and increased at 13 sites; 4 of the 9 decreases and 2 of the 13 increases were statistically significant.

The results therefore indicate that statistically significant declines in monthly average concentrations occurred for PM_{10} mass at 70 percent of the sites, for NO_x at 52 percent of the sites, for PM_{10} nitrate at 48 percent of the sites, and for TSP nitrate at 34 percent of the sites. Other statistical tests (e.g., using daily data) may reveal trends more readily, but the tests tabled here suffice to show that nitrate levels at about half the sites have responded over time to changes in precursor emissions. These temporal changes contrast with the lack of nitrate change occurring between weekdays and weekends. Note, though, that the type of precursor changes that have occurred over time are different from those that occur from weekdays to weekends (with greater VOC than NO_x reductions having occurred over time).

The co-existence of NO_x and nitrate trends is inadequate for inferring causality, as other emission changes have also occurred over time. Of 16 sites with measurements of both NO_x and PM_{10} nitrate, 10 had significantly decreasing NO_x levels. Three of these 10 also had significantly decreasing PM_{10} nitrate; five of the ten had nonsignificantly decreasing nitrate levels. Seven of 16 sites had significantly decreasing nitrate levels. Of those seven, three had increasing NO_x levels, three had significantly decreasing NO_x levels, and one had nonsignificantly decreasing NO_x.

Table 4. Slope, standard error, and signficance levels for regressions of seasonally adjusted monthly-average PM_{10} mass against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error Of Slope (Percent)	Significance Level
El_Capitan_B	96	-0.142	0.066	0.033
Hawthorne	130	-0.21	0.041	0
Redlands-Drb	82	-0.045	0.119	0.704
Ojai-1768Mar	108	-0.471	0.068	0
Norco-Norcnn	84	-0.07	0.108	0.515
Trona-Market	81	-0.341	0.138	0.016
S_Brnrdn-4th	155	-0.284	0.046	0
Fontana-Arrw	167	-0.247	0.042	0
Morro Bay	120	-0.223	0.045	0
Nipomo-S_Wls	79	-0.338	0.11	0.003
Ontario-AP	156	-0.339	0.044	0
Lompoc-S_HSt	84	-0.334	0.09	0
N_Long_Beach	174	-0.274	0.029	0
S_Maria-Libr	131	-0.296	0.041	0
Azusa	179	-0.249	0.038	0
Burbank-WPlm	179	-0.341	0.03	0
Lake_Gregory	115	-0.436	0.067	0
S_Barbr-WCrl	130	-0.309	0.049	0
Banning-Alls	162	-0.221	0.046	0
Perris	142	-0.257	0.058	0
Rvrside-Rubi	180	-0.282	0.04	0
El Toro	178	-0.167	0.031	0
Anaheim-Harb	108	-0.238	0.071	0.001
Hesperia	83	-0.398	0.093	0
Ventura-EMai	119	-0.341	0.06	0
Piru-2mi_SW	155	-0.213	0.05	0
S_L_O-Marsh	144	-0.317	0.044	0
China_Lk-Pwr	79	-0.429	0.147	0.005
S_Clarita-FS	126	-0.268	0.058	0
Simi_V-CchrS	153	-0.35	0.047	0
Ls_Ang-NMain	177	-0.293	0.028	0
Barstow	141	-0.313	0.054	0
Gaviota-ChvE	116	-0.055	0.069	0.424
Jalama Beach	102	0.145	0.086	0.097
Pas_Rob-Snta	81	-0.14	0.083	0.097

Site	Number Of Months	Slope (Percent Per Month)	Standard Error Of Slope (Percent)	Significance Level
Lucrn_Vly-MS	96	-0.598	0.124	0
Gaviota-ChvW	117	-0.06	0.061	0.328
Victrvll-Arm	81	-0.323	0.093	0.001
Atascadero	129	-0.393	0.057	0
Gaviota-GT#A	89	-0.036	0.076	0.636
Gaviota-GT#C	95	-0.083	0.085	0.332
Nipomo-Gudlp	76	-0.311	0.091	0.001
1000_Oaks-Mr	90	0.09	0.09	0.318
El_Rio-Sch#2	141	-0.319	0.051	0
Lancstr-WPnd	114	-0.539	0.104	0
Pt_Conceptin	127	-0.025	0.057	0.661
Van_AFB-STSP	150	-0.241	0.051	0
S_Barbr-UCSB	113	-0.035	0.067	0.605
Arroyo_G-Rlc	60	-0.467	0.108	0
Capitan-LF#1	140	-0.134	0.055	0.015
Capitan-LF#2	95	-0.125	0.065	0.058
Capitan-LF#3	67	-0.516	0.159	0.002
Mojave-Poole	70	0.147	0.142	0.302

Table 5. Slope, standard error, and significance level for regressions of seasonally adjusted monthly-average PM_{10} NO_3 against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error Of Slope (Percent Per Month)	Significance Level
Hawthorne	131	0.118	0.092	0.204
Redlands-Drb	82	0.043	0.273	0.874
Norco-Norcnn	84	-0.217	0.22	0.327
Trona-Market	72	0.074	0.172	0.67
S_Brnrdn-4th	155	-0.158	0.092	0.087
Fontana-Arrw	166	-0.199	0.076	0.01
Ontario-AP	156	-0.255	0.079	0.001
N_Long_Beach	172	0.044	0.063	0.489
S_Maria-Libr	131	-0.475	0.071	0
Azusa	179	-0.108	0.063	0.088
Burbank-WPlm	178	-0.11	0.062	0.076
Lake_Gregory	115	-0.582	0.135	0
Banning-Alls	162	-0.203	0.094	0.033
Perris	142	-0.311	0.11	0.005
Rvrside-Rubi	180	-0.334	0.068	0
El Toro	178	0.099	0.061	0.108
Anaheim-Harb	108	-0.189	0.133	0.156
S_L_O-Marsh	132	-0.679	0.101	0
China_Lk-Pwr	70	-1.116	0.106	0
S_Clarita-FS	126	-0.131	0.123	0.288
Simi_V-CchrS	139	-0.721	0.099	0
Ls_Ang-NMain	177	-0.048	0.057	0.407
Barstow	98	-0.728	0.117	0
El_Rio-Sch#2	124	-0.755	0.101	0
Lancstr-WPnd	85	-0.668	0.159	0

Table 6. Slope, standard error, and significance levels for regressions of seasonally adjusted monthly-average TSP nitrate against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
El_Capitan_B	86	0.241	0.14	0.087
Lancaster	118	0.178	0.068	0.011
Hawthorne	167	-0.193	0.049	0
S_Brnrdn-3rd	60	-0.473	0.308	0.13
Pasadena-SWl	203	-0.188	0.035	0
Ls_Alamts-Or	168	-0.074	0.045	0.098
Pico Rivera	239	-0.134	0.026	0
Trona-Market	151	-0.098	0.053	0.067
Redlands-Grv	72	0.135	0.239	0.574
S_Brnrdn-4th	156	-0.24	0.066	0
La Habra	72	-0.226	0.171	0.191
Fontana-Arrw	216	-0.168	0.036	0
Victrvll-FG	72	0.089	0.165	0.59
Rvrside-Mgnl	238	-0.215	0.037	0
Pas_Rob-10th	90	0.209	0.11	0.061
29_Palm-Adbe	107	-0.027	0.077	0.728
Ontario-AP	87	0.1	0.125	0.425
W_LA-SRbrtsn	60	-0.293	0.241	0.23
Reseda	72	-0.101	0.185	0.586
N_Long_Beach	233	-0.16	0.029	0
S_Maria-Libr	106	0.036	0.088	0.681
Azusa	236	-0.132	0.028	0
Upland-SanBr	206	-0.177	0.033	0
Burbank-WPlm	131	-0.072	0.07	0.312
W_LA-VA_Hosp	174	-0.126	0.044	0.005
Lake_Gregory	126	0.028	0.087	0.746
Banning-Alls	126	-0.084	0.101	0.406
Perris	90	0.081	0.129	0.533

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
Lynwood	238	-0.143	0.03	0
Rvrside-Rubi	239	-0.236	0.036	0
El Toro	126	0.099	0.072	0.171
Anaheim-Harb	192	-0.062	0.041	0.131
Simi_V-CchrI	64	0.434	0.256	0.095
S_L_O-Marsh	60	0.636	0.193	0.002
China_Lk-Pwr	94	0.139	0.093	0.136
Ls_Ang-NMain	236	-0.134	0.029	0
Lennox	70	-0.219	0.175	0.216
Barstow	84	-0.092	0.084	0.28

Table 7. Slope, standard error, and significance level for regressions of seasonally adjusted monthly-average NO_x against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
El_Capitan_B	178	-0.325	0.032	0
Lancaster	118	0.313	0.075	0
Van_AFB-Watt	80	-0.282	0.169	0.098
Hawthorne	168	-0.285	0.042	0
Ojai-1768Mar	82	-0.302	0.083	0
Pasadena-SWl	203	-0.224	0.027	0
Pico Rivera	238	-0.177	0.021	0
Trona-Market	128	0.282	0.149	0.061
S_Brnrdn-4th	154	-0.143	0.03	0
La Habra	72	-0.511	0.096	0
Fontana-Arrw	209	0.099	0.026	0
Nipomo-S_Wls	193	-0.129	0.038	0.001
Lompoc-S_HSt	186	-0.213	0.054	0
Reseda	71	-0.525	0.082	0
N_Long_Beach	231	-0.238	0.02	0
Azusa	240	-0.109	0.021	0
Upland-SanBr	215	0.013	0.019	0.503
Burbank-WPlm	175	-0.136	0.025	0
W_LA-VA_Hosp	177	-0.257	0.037	0
S_Barbr-WCrl	131	-0.225	0.031	0
Lynwood	238	0.014	0.022	0.532
Rvrside-Rubi	237	-0.179	0.019	0
Anaheim-Harb	228	-0.202	0.021	0
Hesperia	89	0.026	0.042	0.531
S_L_O-Lewis	95	-0.159	0.105	0.131
Goleta	143	-0.279	0.04	0
S_L_O-Marsh	228	-0.159	0.017	0
El_Rio-Sch	99	0.013	0.102	0.895

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
S_Clarita-FS	85	-0.108	0.083	0.195
Simi_V-CchrS	169	-0.197	0.035	0
Ls_Ang-NMain	233	-0.201	0.021	0
Lennox	70	-0.617	0.132	0
Barstow	189	0.037	0.033	0.261
Gaviota-ChvE	102	-0.06	0.104	0.57
Jalama Beach	88	1.029	0.243	0
Gaviota-ChvW	107	-0.232	0.086	0.008
Victrvll-Arm	78	-0.05	0.11	0.649
Atascadero	111	-0.431	0.046	0
Gaviota-GT#C	70	0.119	0.126	0.348
1000_Oaks-Mr	84	-0.247	0.103	0.019
El_Rio-Sch#2	93	0.047	0.078	0.545
Lancstr-WPnd	116	-0.108	0.076	0.159
Pt_Conceptin	102	0.17	0.234	0.47
Van_AFB-STSP	104	1.003	0.215	0
S_Barbr-UCSB	101	-0.142	0.115	0.219
Capitan-LF#1	83	-0.204	0.16	0.206
Capitan-LF#2	63	-0.545	0.171	0.002
Mojave-Poole	70	1.178	0.201	0

Table 8. Slope, standard error, and significance level for regressions of seasonally adjusted monthly-average $TSPNO_3/NO_x$ against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
El_Capitan_B	70	0.232	0.172	0.183
Lancaster	118	-0.135	0.097	0.168
Hawthorne	167	0.092	0.054	0.091
Pasadena-SWl	203	0.036	0.033	0.281
Pico Rivera	238	0.044	0.029	0.138
Trona-Market	113	-0.584	0.181	0.002
S_Brnrdn-4th	154	-0.098	0.059	0.098
La Habra	72	0.285	0.161	0.082
Fontana-Arrw	209	-0.269	0.032	0
Reseda	71	0.37	0.2	0.069
N_Long_Beach	231	0.079	0.031	0.01
Azusa	236	-0.021	0.024	0.381
Upland-SanBr	205	-0.185	0.027	0
Burbank-WPlm	131	0.045	0.073	0.537
W_LA-VA_Hosp	174	0.119	0.044	0.008
Lynwood	238	-0.157	0.032	0
Rvrside-Rubi	236	-0.052	0.033	0.118
Anaheim-Harb	192	0.086	0.038	0.025
S_L_O-Marsh	60	0.543	0.19	0.006
Ls_Ang-NMain	231	0.07	0.031	0.025
Lennox	70	0.398	0.172	0.023
Barstow	78	-0.123	0.117	0.298

Table 9. Slope, standard error, and significance level for regressions of seasonally adjusted monthly-average $PM_{10}NO_3/NO_x$ against month. Sites are restricted to those in the South Coast, South Central Coast, and Mojave Desert Air Basins with 5 or more years of data.

Site	Number Of Months	Slope (Percent Per Month)	Standard Error of Slope (Percent Per Month)	Significance Level
Hawthorne	131	0.316	0.095	0.001
S_Brnrdn-4th	153	-0.013	0.083	0.873
Fontana-Arrw	164	-0.25	0.067	0
N_Long_Beach	171	0.322	0.062	0
Azusa	179	0.056	0.058	0.338
Burbank-WPlm	173	0.01	0.065	0.88
Rvrside-Rubi	177	-0.121	0.064	0.061
Anaheim-Harb	108	0.213	0.122	0.082
S_L_O-Marsh	132	-0.575	0.103	0
S_Clarita-FS	85	-0.028	0.175	0.871
Simi_V-CchrS	136	-0.499	0.1	0
Ls_Ang-NMain	172	0.147	0.063	0.02
Barstow	90	-0.664	0.149	0
El_Rio-Sch#2	78	-0.683	0.173	0
Lancstr-WPnd	85	-0.521	0.219	0.02

Table 10. 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 seasonally adjusted monthly-average PM_{10} mass, TSP mass, $PM_{10}NO_3$, $TSPNO_3$, NO_x, $PM_{10}NO_3/NO_X$, and $TSPNO_3/NO_x$ concentrations. Sites were included if they had 5 or more years of data.

Species	Decreasing Trends		Increasing Trends	
	No. of Sites	No. Significant	No. of Sites	No. Significant
$PM_{10}NO_3$	20	12	5	0
$TSPNO_3$	25	13	13	1
NO_X	34	25	14	5
$PM_{10}NO_3/NO_X$	9	5	6	2
$TSPNO_3/NO_X$	9	4	13	2
PM_{10}	50	37	3	0

Trends were also examined for monthly-average concentrations of selected species from six CADMP: Long Beach, downtown Los Angeles, and Azusa in the Los Angeles area, and Santa Barbara, Bakersfield, and Sacramento. More species were measured at the CADMP sites than at routine monitors, but the period of record was shorter (mid-1988 through mid-1994). The method for computing seasonally-adjusted monthly averages was described above. Results are shown in Tables 11 through 13 for ammonia, NH_3/NO_x, and NH_3/SO_2. No statistically significant ($p<0.01$) trends were found for ammonia (Table 11). However, statistically significant increasing trends occurred for the ratio of NH_3/SO_2 at Azusa, Bakersfield, and downtown Los Angeles (Table 13); this ratio also increased at Long Beach ($p<0.05$). These results indicate that ammonia levels did not change, whereas SO_2 concentrations declined.

Table 11. Regression coefficients for seasonally-adjusted monthly-average NH_3 for the period mid-1988 through mid-1994.

Site	Number Of Monthly Observations	Slope (%/Month)	R^2	Standard Error Of Slope (%/Month)	Significance Level
Azusa	69	-0.050	<0.001	0.195	0.799
Bakersfield	69	-0.135	0.007	0.194	0.490
Los Angeles	69	0.033	<0.001	0.203	0.872
Long Beach	69	0.019	<0.001	0.279	0.947
Sacramento	66	-0.543	0.093	0.212	0.0129
Santa Barbara	30	0.025	<0.001	0.493	0.960

Table 12. Regression coefficients for seasonally-adjusted monthly-average NH_3/NO_x for the period mid-1988 through mid-1994.

Site	Number Of Monthly Observations	Slope (%/Month)	R^2	Standard Error of Slope (%/Month)	Significance Level
Azusa	69	0.333	0.035	0.215	0.126
Bakersfield	38	-0.498	0.082	0.278	0.081
Los Angeles	69	0.303	0.018	0.275	0.276
Long Beach	69	0.094	0.003	0.218	0.666
Sacramento	57	-0.643	0.025	0.541	0.240
Santa Barbara	25	-0.583	0.013	1.045	0.582

Table 13. Regression coefficients for seasonally-adjusted monthly-average NH_3/SO_2 for the period mid-1988 through mid-1994.

Site	Number Of Monthly Observations	Slope (%/Month)	R^2	Standard Error of Slope (%/Month)	Significance Level
Azusa	67	1.036	0.102	0.380	0.008
Bakersfield	65	1.048	0.118	0.361	0.005
Los Angeles	67	0.936	0.186	0.242	<0.001
Long Beach	66	0.785	0.063	0.380	0.043
Sacramento	64	-0.190	0.003	0.449	0.674
Santa Barbara	30	-1.549	0.091	0.924	0.105

Principal Component Analysis

Since PM nitrate concentrations showed so little variation from weekdays to weekends, few or no clear linkages to the ambient concentrations of other species, and weak temporal trends, we attempted to relate nitrate concentrations to other variables using a multivariate statistical approach. The specific method used was principal component analysis (PCA), applied to combined CADMP and routine CARB data. Eigenvalues exceeding one were retained, and orthogonal solutions were employed (PCA permits other choices for the number of components to retain, as well as allowing nonorthogonal solutions, and the literature includes much discussion of optimal choices. The choices used here represent commonly accepted procedures).

Figure 59 displays the results for Los Angeles, Long Beach, Azusa, and Santa Barbara (the last site is outside the SoCAB but in southern California; all other CADMP sites were in northern California or the Central Valley). The correlations among species were generally consistent among the four sites. All four sites showed high correlations among the primary pollutants: CO, NO, NO_2 (technically, this measurement of NO_2 includes interferants such as PAN and HNO_3), NO_x, the CADMP measurement of NO_2, and, to a lesser degree, NH_3 and SO_2 (Figure 59, Factor 1). Ozone and nitric acid were associated at all four sites (Factor 2); higher concentrations of these species were associated with higher temperatures and radiation at all three of the SoCAB sites. Also at the three SoCAB sites, $PM_{2.5}$ NH_4, $PM_{2.5}$ NO_3, and $PM_{2.5}$ SO_4 were associated with each other as Factor 3. However, at Santa Barbara, the groupings of variables on the second and third factors differed from those at the SoCAB sites, with radiation and temperature being a third factor (not associated with ozone and nitric acid) and particulate nitrate, sulfate, and ammonium positively correlated with ozone and nitric acid. In all cases, the secondary species appear grouped separately from the primary species, indicating that higher concentrations of secondary species did not relate directly to higher concentrations of primary species. Moreover, in the SoCAB, higher PM nitrate concentrations varied with sulfate and ammonium concentrations, rather than with ozone and nitric acid (reflecting the opposing temperature dependencies of nitrate and nitric acid). All sites showed correlations between PM_{10} Cl and PM_{10} Na, which are usually linked to sea salt aerosol, and the sites showed varying associations of coarse nitrate (PM_{10} nitrate minus $PM_{2.5}$ nitrate) with this last factor.

Quantitative source contributions will not be inferred from the PCA. Rather, the results are taken as a qualitative indication that PM nitrate concentrations vary in a complex way with meteorological factors and the concentrations of other secondary species, and cannot be directly linked to primary species concentrations in a simple cause-effect relation.

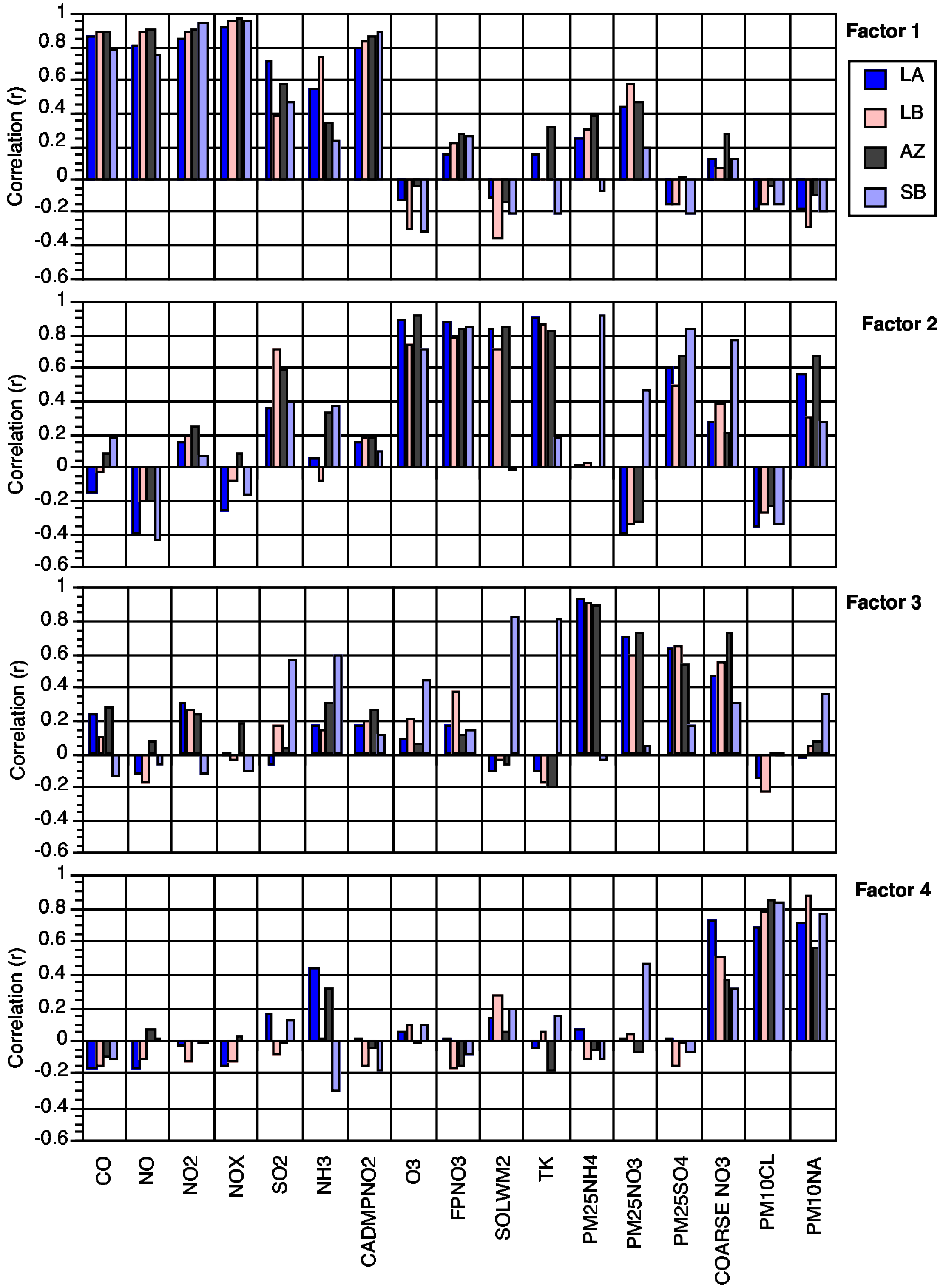


Figure 59.Orthogonal factor analyses for CADMP sites in southern California (Los Angeles, Long Beach, Azusa, and Santa Barbara). The CADMP measurement of NO_2 was based on analysis of nitrite on filter pack samples. “FPNO3” is a measure of nitric acid (including dissociated ammonium nitrate). “SOLWM2” and “TK” denote radiation and temperature, respectively.