Attachment 1

Background Information on Federal RFG Oxygenate Waiver Impacts on Particulate Matter

Prepared by

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Contribution of Ammonium Nitrate to PM10 and PM2.5 in California

PM10 and PM2.5 concentrations vary widely throughout California. In general, both the highest 24-hour and annual average concentrations are found at sites in the South Coast Air Basin and San Joaquin Valley Air Basin, which are both currently designated as serious nonattainment for the federal PM10 standards. These two air basins, along with San Diego, are expected to be designated as nonattainment for the federal PM2.5 standard as well in 2004. However, relatively high 24-hour measurements are also found in the Sacramento Valley Air Basin, San Francisco Bay Area Air Basin, and certain parts of the Mountain Counties Air Basin. The highest PM10 and PM2.5 concentrations occur between mid-November and mid-February when several source contributions are superimposed on each other. This seasonal pattern is typical for most of California but is most pronounced in the San Joaquin Valley Air Basin. The exception is the South Coast Air Basin, where high values occur throughout the year.

Elevated particulate matter (PM) concentrations result from a combination of emissions, transport, transformation, and accumulation of pollutants. Atmospheric PM is a complex mixture of a variety of primary and secondary particles differing in size and chemical composition. Primary particles are directly emitted by sources while secondary particles form from directly emitted gases by transformation in the atmosphere. The relative importance of primary and secondary particles depends on many factors, including precursor emissions, atmospheric chemistry, and meteorology. Secondary ammonium nitrate comprises a large fraction of PM10 and even a larger fraction of PM2.5 mass in California. The two serious federal PM10 nonattainment areas, South Coast and San Joaquin Valley, have the highest concentrations of ammonium nitrate in California. Tables 1 and 2 demonstrate the significant fraction of ammonium nitrate in PM10 and PM2.5 mass, respectively. Table 1, except where noted, is based on PM10 chemical composition data collected as part of the California Regional PM10/PM2.5 Air Quality Study (CRPAQS). The annual average values in Table 2 are based on routine PM2.5 chemical composition data, while 24-hour exceedance data are based on routine and CRPAQS data combined. Roughly 20 to 30 percent of the annual average PM10 mass and 30 to 40 percent of the annual average PM2.5 mass is ammonium nitrate (Tables 1 and 2). Basin-high annual average PM10 ammonium nitrate concentrations ranged from 11 μg/m^3 in the San Joaquin Valley to 27 μg/m^3 in the South Coast. The ammonium nitrate fraction is even larger on the peak PM days and was found to contribute up to 57 percent of PM10 mass and 84 percent of PM2.5 mass. Peak 24-hour average PM10 ammonium nitrate levels in the South Coast Air Basin and the San Joaquin Valley Air Basin reached over 100 μg/m^3. With respect to PM2.5, ammonium nitrate concentrations alone can exceed the federal PM2.5 standards.

Table 1. PM10 Ammonium Nitrate Fractions (Based on 2000 CRPAQS PM10 Chemical Composition Data)

Basin	Site Name	2000 Annual Average		PM10 Exceedance Days		
		Conc (μg/m^3)	% of PM10 Mass	# of Days	Ammonium Nitrate	
					Max Conc (μg/m^3)	Max % of PM10 Mass
SJV	Bakersfield-Golden	10	22	1	98	47
SJV	Corcoran-Patterson	10	24			
SJV	Fresno Drummond	10	24	2	63	38
SJV	Hanford-Irwin St.	11	27	1	75	48
SJV	Modesto-14th St.	7	23			
SJV	Oildale-Manor	11	28	1	112	57
SJV	Visalia Church St.	11	25			
SC	Riverside-Rubidoux	27*	34*	3*	110	52*

* Based on 1995 PTEP monitoring conducted in the South Coast.

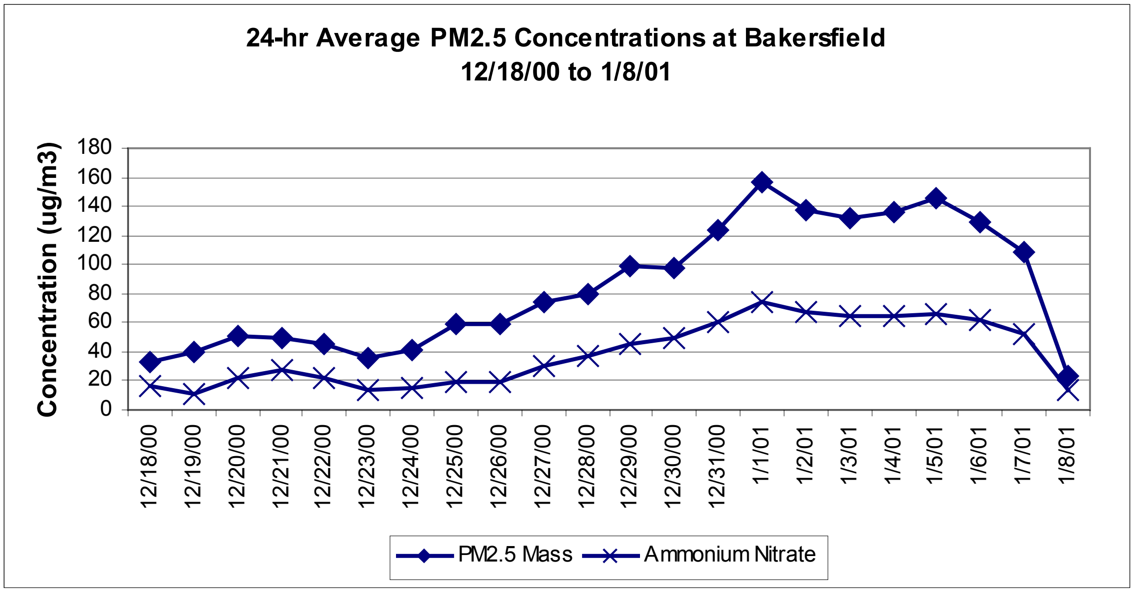
Table 2. PM2.5 Ammonium Nitrate
(Based on Routine and CRPAQS PM2.5 Chemical Composition Data)

Basin	Site Name	6/1/01-5/31/02 Annual Average		PM2.5 Exceedance Days			
		Conc ($\mu g/m^3$)	% of PM2.5 Mass	# of Days	Ammonium Nitrate		
					Max Conc ($\mu g/m^3$)	% of PM2.5 Mass	
						Avg	Max
SC	Riverside-Rubidoux	15	44	8	51	59	64
SD	El Cajon	6	41	0			
SFB	San Jose-4th Street	4	24	0			
SJV	Bakersfield-California	9	33	17	78	58	67
SJV	Oildale-Manor	9	42*	8	73	61	84
SJV	Fresno-1st Street	9	32	25	72	39	73
SV	Sacramento-13th St.	3	34*	3	53	43	59

* Based on 2000 CRPAQS data.

Elevated PM concentrations can sometimes occur as isolated and localized events, but most of the time they result from a buildup of concentrations throughout the region to yield the highest PM concentrations. Figure 1 illustrates a buildup and dissolution of PM2.5 mass and ammonium nitrate concentrations at Bakersfield between December 18, 2000 and January 8, 2001. This episode resulted in record high PM10 and PM2.5 concentrations throughout Central California. Ammonium nitrate was a substantial fraction of the PM mass comprising 50 to 70 percent of the PM2.5 mass at most sites in the San Joaquin Valley. This episode represented the highest concentrations included as part of the San Joaquin Valley Air Pollution Control District's recently adopted PM10 plan and illustrates the significant role of ammonium nitrate both in the buildup and resultant exceedances of PM standards in the San Joaquin Valley.

Figure 1



Chemical Formation of Ammonium Nitrate from NOx Emissions

As discussed above, a substantial fraction of both the PM10 and PM2.5 mass in California is comprised of secondary ammonium nitrate. The formation of secondary ammonium nitrate begins with the oxidation of NOx into nitric acid. The nitric acid then reacts with gaseous ammonia to form ammonium nitrate. NOx can be oxidized into nitric acid through both daytime and nighttime reactions involving the hydroxyl radical and ozone respectively. Although VOCs can play a role in the oxidation of NOx to nitric acid, studies in the San Joaquin Valley have shown that ammonium nitrate is most responsive to reductions in NOx emissions, with minimal response to changes in VOC emissions.

Chemical Formation of Secondary Organic Aerosols from VOC Emissions

A portion of PM10 and PM2.5 in California also results from the formation of secondary organic aerosols due to the oxidation of VOCs. Atmospheric chemical reactions involving VOC species with at least seven carbon atoms can produce secondary organic aerosols. The reaction products can either form new particles, or condense onto existing particles. This process is expected to be most active during periods of high photochemical activity. Because peak PM10/PM2.5 concentrations are not well correlated with peak ozone, secondary organic aerosols do not generally comprise a large fraction of the measured carbon in either the San Joaquin Valley or the South Coast. Estimates of the fraction of carbon which is secondary in origin ranges from 20 percent of peak 24-hour exceedances in the San Joaquin Valley, to 20 to 30 percent of the annual average in the South Coast. Semi-volatile VOC species can also be directly adsorbed onto existing particles under low temperature, high humidity conditions.

Role of Carbon Monoxide in PM Formation

The simplest carbon containing molecule in the atmosphere, carbon monoxide (CO), participates in the conversion of free radicals (hydroxyl radical to hydroperoxyl radical) that enhance the oxidation of NOx to nitric acid. However, there are several other paths to the same radical conversion and the role of CO in the oxidation of NOx to nitric acid is minor in the polluted atmosphere. CO does not play a direct role in the oxidation of VOCs into secondary organic aerosls. Thus the role of CO in producing secondary particulate matter in the polluted atmosphere is minor or negligible. To our knowledge, no PM10 plan has ever included CO controls for PM.

Impact of Changes in NOx and VOC Emissions on PM10 and PM2.5 Concentrations in California

The San Joaquin Valley and South Coast have recently prepared PM10 attainment plans that demonstrate the relationship between emission changes and resulting PM concentrations and the impacts of control strategies on achieving the national ambient air quality standards for PM10. The potential impact of changes in NOx and VOC emissions on the PM10 concentrations in these two areas was estimated by following the attainment demonstration procedures contained in each plan. In the San Joaquin Valley the 24-hour PM10 standard is the most difficult to attain, while in the South Coast it is the annual standard. Therefore, the highest 24-hour design value at Bakersfield-Golden, with a 24-hour average concentration of 205 $\mu g/m^3$, was selected to evaluate the potential impacts on 24-hour concentrations, while the highest annual design value at Riverside-Rubidoux of 56.8 $\mu g/m^3$ was selected to evaluate an annual impact.

The impact on the peak 24-hour PM10 value in the San Joaquin Valley was estimated by closely following the procedure outlined in the San Joaquin Valley plan, which used both CMB modeling with grid-based photochemical aerosol chemistry modeling analysis (UAM-Aero), combined with proportional rollback to demonstrate attainment. The CMB modeling provided source apportionment for primary particles. The grid-based photochemical model provided a conversion factor for precursors into secondary particles (1.5 NOx to 1 nitrate proportionality ratio) that was then used in the proportional rollback analysis for ammonium nitrate. Rollback calculations were used to determine future compliance with the 24-hour standard by calculating the effect of emission reductions predicted for the major source categories. The incremental impact of changes in NOx and VOC emissions on PM10 due to oxygenated gasoline was estimated by changing the projected NOx and VOC emissions in the rollback analysis by 10 tons per day. The results show that while changing NOx emissions by 10 tons per day would change the peak 24-hour PM10 concentration by 1.5 ug/m^3, changing VOC emissions by the same amount would only result in a 0.14 µg/m^3 change in PM10.

The impact on the annual average PM10 concentration in the South Coast Air Basin was estimated by applying a simple linear rollback approach. Annual average PM10 total mass and composition was predicted using the UAM-LT model applied to a full year of data. The predicted PM composition data from the model results and emissions data from the 2002 Almanac were used to estimate a simple linear response to a 10 ton per day change in either VOC or NOx emissions. A conversion factor of 1 NOx to 1 nitrate was assumed in the analysis. The resulting annual average impacts were then reduced by one third as the waiver for the federal oxygenate standard would only apply for eight months of the year. The change in annual PM10 concentration from a 10-ton per day change in NOx emissions in the South Coast was again an order of magnitude larger than from the same 10 ton per day change in VOC emissions. Table 3 shows the incremental impact on PM10 concentrations in the San Joaquin Valley and the South Coast from a 10 ton per day change in NOx or VOC emissions.

Table 3. PM10 Concentration Response to 10 ton per day change in NOx and VOC Emissions

Site	PM10 Concentration Change from NOx (ug/m^3)	PM10 Concentration Change from VOC (ug/m^3)
Bakersfield Golden	1.5	.14
Riverside Rubidoux	.12	.011

Emission reductions that lower PM10 concentrations will also lower PM2.5 concentrations. Because almost all of the ammonium nitrate and secondary organic carbon can be found in the PM2.5 size fraction, the results presented for PM10 also are applicable for PM2.5.

Role of NOx Controls in Attaining PM10 and PM2.5 Standards

Both the San Joaquin Valley and South Coast attainment plans indicate that a substantial fraction of the PM10 mass is secondary ammonium nitrate formed in the atmosphere from photochemical reactions involving precursor gases. Both PM10 attainment plans indicate that reducing NOx emissions has the largest beneficial impact on ambient PM10 levels, and both plans rely strongly on NOx controls to demonstrate attainment. Although modeling in the San Joaquin Valley indicates that VOC controls are not effective in reducing secondary ammonium nitrate, they do result in a small decrease in PM10 mass due to reduction in condensable PM10 emissions from these organic compounds. Since the VOC related reductions are very small compared to NOx related reductions, the decrease in VOC emissions due to oxygenated gasoline will have a much smaller impact on PM10 concentrations than the corresponding increase in NOx emissions. The impact of NOx and VOC emissions on PM concentrations is reflected in the PM reductions projected in the attainment plans. In the San Joaquin Valley, approximately 19 $\mu g/m^3$ in PM10 reductions came from NOx controls and 2 $\mu g/m^3$ from VOC related controls (Table 4). In the South Coast, approximately 13 $\mu g/m^3$ in PM10 reductions came from NOx controls and only 0.2 $\mu g/m^3$ from VOC related controls (Table 5).

Table 4. Peak 24-hour Exceedance Composition and Controls

Site	Year	Total PM10 Concentration (ug/m^3)	Ammonium Nitrate (ug/m^3)	Secondary Organics (ug/m^3)*	Ammonium Sulfate (ug/m^3)	Other Primary (ug/m^3)
Bakersfield Golden	2001	205	95.39	6.88	7.02	95.71
	2010	152	75.90	4.90	5.10	65.60

* Assumes 50% of the mobile source and other organic carbon categories is secondary and responds to VOC control.

Table 5. Peak Annual Exceedance Composition and Controls

Site	Year	Total PM10 Concentration (ug/m^3)	Ammonium Nitrate (ug/m^3)	Secondary Organics (ug/m^3)*	Ammonium Sulfate (ug/m^3)	Other Primary (ug/m^3)
Riverside Rubidoux	1995	56.8	24.38	2.10	3.86	26.46
	2006	47.6	15.35	1.98	4.27	26.00
	2010	45.0	11.73	1.89	4.14	27.24

* Assumes that 30% of the organic carbon is secondary and therefore responds to VOC control - this is the percentage assumed in the 24-hour rollback analysis used in the South Coast attainment demonstration modeling.

Impact of Emission Changes on PM10 and PM2.5 Attainment

There are several sites in both the San Joaquin Valley and the South Coast attainment plans that demonstrate attainment of the PM10 standards by only small margins. For example, the modeling for Bakersfield-Golden predicts a PM10 concentration of 152 $\mu g/m^3$ in the 2010 attainment year, with a value of 154.5 $\mu g/m^3$ considered nonattainment. In the South Coast, the modeling predicts a PM10 concentration of 50.4 $\mu g/m^3$ at Ontario in the 2006 attainment year, with a value of 50.5 $\mu g/m^3$ considered nonattainment. Therefore, a waiver from the federal oxygenate requirement would provide an additional margin of safety in assuring attainment of the federal PM10 standards in these areas as well as facilitate more expeditious attainment.

Moreover, in order to attain the federal PM2.5 standards, significant further emission reductions beyond those specified for PM10 will be needed. For example, even with planned controls, the South Coast attainment plan estimates that Fontana will be 80 percent above the federal PM2.5 standard in 2010. Although future PM2.5 concentrations were not addressed in the San Joaquin Valley PM10 attainment plan, the impacts of controls included in the PM10 plan on PM2.5 suggest that the San Joaquin Valley could also be approximately 70 to

80 percent above the federal 24-hour PM2.5 standard in 2010. Secondary ammonium nitrate is the largest component of the PM2.5 mass, often constituting more than 50 percent of the mass. Therefore, additional reductions in NOx emissions will be essential in achieving the federal PM2.5 standards in these areas.