

PM AIR QUALITY IN THE SOUTH COAST AIR BASIN: WHAT HAS CHANGED SINCE 1985?

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ABSTRACT

PM air quality in the South Coast Air Basin (Basin) of Southern California has improved significantly since the inception of PM₁₀ monitoring in 1985. A clear downtrend in annual average PM concentrations has been observed over the period 1985-2007 resulting from South Coast Air Quality Management District (SCAQMD, or District), state, and federal regulatory efforts to improve PM air quality. Four years of special monitoring data were investigated and the results show that chemical components have declined at different rates. During the period 1986-1995, organic carbon, crustal, and sulfate drove the PM reduction for both downtown Los Angeles and Rubidoux sites, while ammonium and nitrate drove the PM reduction during the period 1995-1998. Organic carbon and elemental carbon drove the improvement of PM_{2.5} during the period of 1998-2005 at downtown Los Angeles and nitrate, organic carbon, elemental carbon and crustal component drove the improvement at Rubidoux.

1. INTRODUCTION

Since Los Angeles experienced its first recorded smog in 1943, much effort has been dedicated to improve air quality and thereby to protect public health in the Basin. The District's Air Quality Management Plan (AQMP) comprises an integrated blue print for attaining federal clean air standards, and is regularly evaluated and revised for the Basin. This planning and implementation effort has resulted in dramatic reductions for all criteria air pollutants in the Basin and the region is now on course for attainment of federal standards.

Basin PM₁₀ monitoring was initiated in 1985. Since then, significant improvement in PM air quality has been observed in the Basin. PM is a multicomponent criteria air pollutant which

includes sulfate, nitrate, ammonium, organic carbon, elemental carbon, and trace metals. Therefore, it is important to investigate whether major chemical components have declined at the same rate as the total mass. This paper also determines and discusses which chemical components of PM drove the improvement of PM air quality over the 22-year period.

2. PM DATABASE

The District has an extensive PM₁₀ and PM_{2.5} monitoring network; that is designed specifically to monitor progress toward attainment of PM standards. From this PM₁₀ and PM_{2.5} mass data, a PM mass trend in the Basin can be determined; however, trends of chemical components such as ammonium, nitrate, sulfate, organic carbon, elemental carbon, crustal components and other trace metals cannot be determined. Therefore, chemical species concentrations from four special PM monitoring programs, 1986, 1995, 1998-1999, and 2004-2006, were used in the analysis. The database description follows.

2.1 1986, One-Year Special Monitoring Data

The Environmental Quality Laboratory (EQL) of the California Institute of Technology conducted PM₁₀ sampling throughout 1986 in the Basin. 24-hour samples were taken every sixth day from January to December 1986 at nine locations. PM₁₀ was sampled at all sites; PM_{2.5}, however, was sampled only at the downtown Los Angeles site. Total mass and 41 species (34 trace elements, organic and elemental carbon, and key ions) were analyzed. A more detailed description of the monitoring sites, sampling schedule, and sampling analysis can be found in Solomon et al. (1989).

2.2 1995, PTEP Enhanced Ambient Air Monitoring Program

In 1995, a special one-year particulate monitoring program was conducted in the Basin as part of the PM₁₀ Technical Enhancement

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Program (PTEP). PM₁₀ and PM_{2.5} 24-hr average samples were measured at five monitoring stations (downtown Los Angeles, Anaheim, Diamond Bar, Fontana, and Rubidoux) in the Basin and at one background station at San Nicolas Island. Sampling was scheduled once every six days from January to March, except for the Rubidoux site that was sampled once every three days. PM_{2.5} and PM₁₀ mass and 43 individual chemical species were analyzed. Details of the ambient measurements, spatial and temporal variations, nitrate and organic carbon artifacts can be found in Kim et al (1999, 2000a, 2000b, and 2001).

2.3 1998-1999, TEP 2000 Enhanced Ambient Air Monitoring Program

As a sequel to the PTEP program, the District conducted a comprehensive program to characterize the ozone and PM problem in the Basin for the 2000 AQMP. Under this Technical Enhancement Program for the 2000 AQMP revision (TEP 2000), a one-year special monitoring program was conducted in the Basin from August 1998 through July 1999 at eight sites. A one-in-three day sampling schedule was conducted from August 1998 to January 1999. Sampling frequency was decreased to once every six days from February 1999 to July 1999. PM₁₀ and PM_{2.5} mass and the same 43 chemical species as were determined in the PTEP program were analyzed using the same analytical methods.

2.4 2004-2006 MATES III Program

A 2-year special particulate monitoring program was initiated in April 2004 as part of the Multiple Air Toxics Exposure Study III (MATES III). The MATES III is a toxic air contaminants monitoring and evaluation study conducted in the Basin and is part of the District's Environmental Justice Initiative. Under MATES III, 24-hour PM_{2.5} mass and 43 chemical species were measured on a one-in-three day sampling schedule at ten sites.

3. RESULTS AND DISCUSSIONS

3.1 PM₁₀ and PM_{2.5} Mass Trend Based on District Routine Mass Data

Significant improvement in PM₁₀ air quality has been observed in the Basin since the inception of PM₁₀ monitoring in 1985. Figure 1 shows the Basin maximum annual average PM₁₀

concentrations for the 22-year period, and clearly indicates a downward trend. Figure 2 shows the Basin maximum annual average PM_{2.5} concentrations over the period, 1999-2007, and shows a clear downward trend. (Note: the Mira Loma air monitoring site was commissioned in 2005). No adjustment has been made to the trends to account for annual weather variability.

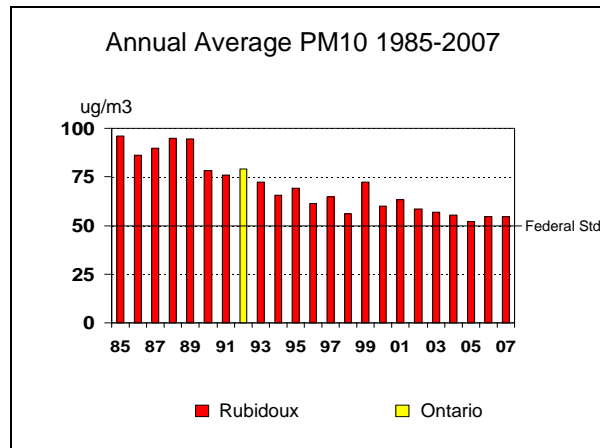


Figure 1. Basin maximum annual average PM₁₀

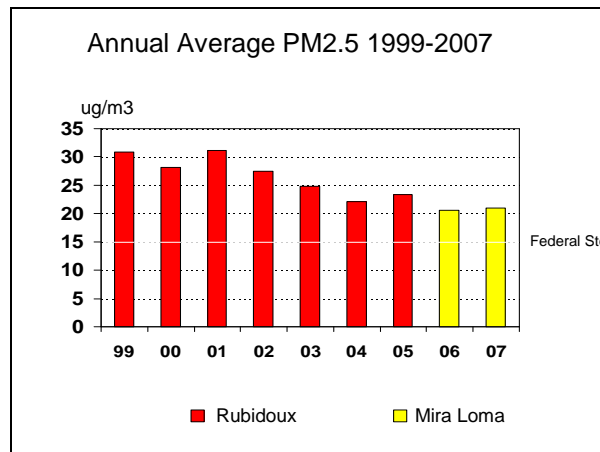


Figure 2. Basin maximum annual average PM_{2.5}

3.2 Trends of PM₁₀ and PM_{2.5} Chemical Components Based on Four Years of Special Monitoring Data

Chemically speciated PM₁₀ and PM_{2.5} data at two sites (downtown Los Angeles and Rubidoux) were used for the analysis. EQL measured PM_{2.5} data for 1986 is available only for downtown Los Angeles. 1986 PM_{2.5} data for Rubidoux were extracted from Christoforou et al (2000), which discussed trends in fine particle levels during 1982-1993 using three years of data (1982, 1986 and 1993).

Annual average PM₁₀ and PM_{2.5} concentrations for ammonium, nitrate, sulfate, organic carbon (OC), elemental carbon (EC) and crustal component are summarized in Tables 1 and 2, and shown in Figures 3 and 4, respectively. Crustal component is a sum of oxides of trace metals; aluminum, silicon, calcium, manganese, and iron. Organic carbon in 2005 was not used in the analysis because measured ambient OC is believed to be significantly biased. The flow rate of OC measurement (6.7 lpm) for the new PM sampler SASS, used in MATES III, was approximately 3 times slower than that (20 lpm) of the Multi-Channel Fine Particulate (MCFP) sampling system, which was designed to properly account for positive organic artifact formation during sampling for the PTEP and TEP 2000 programs. Slower flow rate in the SASS sampler reduces pressure drop through the sampler and

Table 1. Annual average PM₁₀ concentrations for the three years observed at Downtown LA and Rubidoux.

Annual Average PM10						
	Downtown LA			Rubidoux		
	1986	1995	1998	1986	1995	1998
Mass	60.21	51.14	48.83	87.38	76.83	64.42
NH4	3.56	4.71	2.37	5.65	6.58	3.72
NO3	8.76	11.55	9.31	17.47	19.35	14.36
SO4	5.69	5.19	4.43	5.11	4.39	3.63
OC	13.29	7.48	7.46	11.03	8.96	8.22
EC	4.25	4.23	3.46	2.78	3.54	2.98
Crustal	10.99	9.10	10.88	24.15	21.60	22.91

Table 2. Annual average PM_{2.5} concentrations for the four years observed at Downtown LA and Rubidoux.

Annual Average PM2.5								
	Downtown LA				Rubidoux			
	1986	1995	1998	2005	1986	1995	1998	2005
Mass	36.79	30.32	23.55	19.48	43.80	39.75	36.59	22.87
NH4	3.36	4.55	1.92	2.56	5.90	6.77	3.28	3.10
NO3	4.79	8.47	5.51	5.71	13.40	16.12	10.75	8.17
SO4	5.15	4.63	3.65	3.84	4.60	3.53	3.07	3.41
OC	11.43	5.96	5.45		7.93	5.56	5.15	
EC	4.03	3.81	3.05	2.10	2.50	3.25	2.59	1.77
Crustal	1.33	1.03	1.29	1.45	2.50	2.05	4.12	1.67

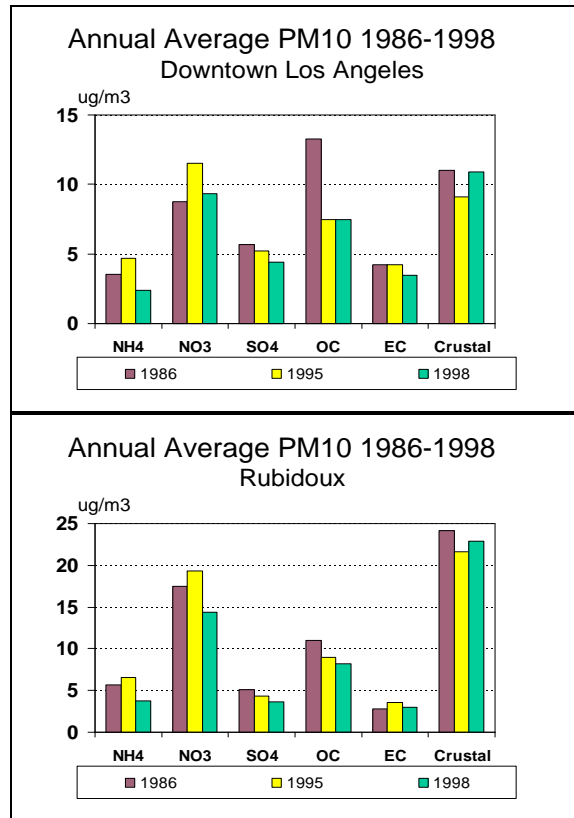


Figure 3. PM₁₀ chemical components at LA and Rubidoux.

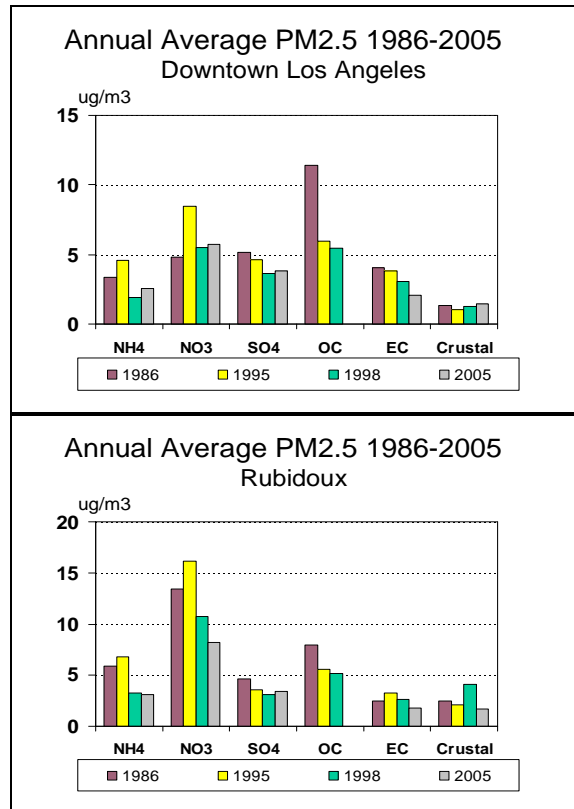


Figure 4. PM_{2.5} chemical components at LA and Rubidoux.

increases the adsorption of organic vapor on the filter medium; therefore, OC measured by SASS sampler is significantly higher than that measured by MCFP sampler.

As shown in Figures 3 and 4, each chemical component declines at a different rate; these figures show that the decreases between 1986 and 1995, 1995 and 1998 are different from the decrease between 1998 and 2005.

Organic carbon, crustal and sulfate drove the improvement in PM₁₀ and PM_{2.5} during the period of 1986-1995, while ammonium and nitrate were most responsible for the major improvement in PM₁₀ and PM_{2.5} during the period of 1995-1998. Sulfate and OC also declined slightly during this period. From 1998 to 2005, PM_{2.5} ammonium, nitrate, and sulfate increased slightly, and EC decreased at downtown Los Angeles. During the same period, sulfate increased slightly while nitrate, EC and crustal components decreased at Rubidoux. Decreases of EC in downtown Los Angeles, and nitrate, EC and crustal in Rubidoux are not sufficient to explain PM_{2.5} mass reduction from 1998 to 2005. Organic carbon that is not included in the analysis must have declined significantly, by about 3 ug/m³ to explain the mass reduction properly for both downtown Los Angeles and Rubidoux. Overall, OC and EC drove the improvement of PM_{2.5} during the period of 1998-2005 at downtown Los Angeles and nitrate, OC, EC and crustal component drove the improvement at Rubidoux.

Emission reductions from 1985 to 2005 are shown in Figure 5. ROG, NOx and SOx emissions are taken from 2007 Almanac of the California Air Resources Board (CARB, 2007) and PM₁₀ crustal, diesel, and mobile source emissions are taken from the 1997 AQMP (Bassett *et al*, 1996). The more than 50% reduction in SOx emissions depicted in Figure 5 is reflected in reduced sulfate concentrations over the past 19 years; however the amount of sulfate reduction is not as large. Hoggan *et al*, (1993) showed that the nitrate and sulfate reductions over the seven years of 1985-1992 were not statistically significant. This can be explained by two reasons, limited availability of ammonia and primary sulfate. In 1986, ammonia in the western portion of the Basin might have not been sufficient to neutralize sulfuric acid in downtown Los Angeles. In contrast, the primary sulfate portion must have been significant, so reduction in SOx emissions is not directly reflected in the sulfate concentration.

Nitrate and ammonium concentrations for both PM₁₀ and PM_{2.5} increased during the period 1986-1995. However, nitrate concentrations show

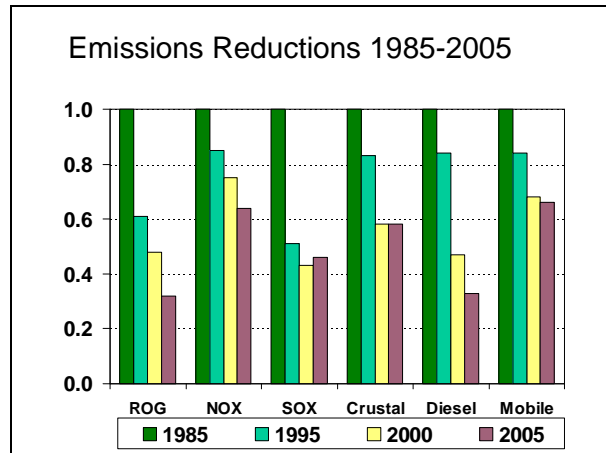


Figure 5. Emissions reductions for gaseous pollutants.

a decrease from 1986 to 1998 for PM₁₀ and from 1986 to 2005 for PM_{2.5} at Rubidoux, but a slight increase at downtown Los Angeles. This site-specific nitrate trend and increase of ammonium and nitrate from 1986 to 1995 can be explained by three processes of ammonia availability in the Basin:

1) It is well known that ammonia is abundant at Rubidoux because of the upwind intense array of dairy farm ammonia sources; however, this ammonia is generally not enough to neutralize all available nitric acid in the rest of the Basin (Kim *et al*, 2000a). This can be confirmed by the PM_{2.5} to PM₁₀ ratio shown in Table 3. The nitrate ratio at Rubidoux is greater than at downtown Los Angeles, which implies that fine ammonium nitrate is formed more readily at Rubidoux than at downtown Los Angeles. In an area of excess ammonia such as

Table 3. PM_{2.5} to PM₁₀ ratios at Los Angeles and Rubidoux.

PM _{2.5} /PM ₁₀ Ratios						
	Downtown LA			Rubidoux		
	1986	1995	1998	1986	1995	1998
Mass	0.61	0.59	0.48	0.50	0.52	0.57
NH ₄	0.94	0.97	0.81	1.04	1.03	0.88
NO ₃	0.55	0.73	0.59	0.77	0.83	0.75
SO ₄	0.91	0.89	0.82	0.90	0.80	0.85
OC	0.86	0.80	0.73	0.72	0.62	0.63
EC	0.95	0.90	0.88	0.90	0.92	0.87
Crustal	0.12	0.11	0.12	0.10	0.09	0.18

Rubidoux, reduction in sulfate has no effect on nitrate concentration; however, in an ammonia-

limited area such as downtown Los Angeles, reduction in sulfate production due to SO_x emissions reductions leads to increase of nitrate concentration. One mole of sulfate reduction frees two moles of ammonia to react with nitric acid, forming two moles of ammonium nitrate. Therefore, a reduction of SO_x results in an increase of nitrate in downtown Los Angeles.

2) The PM_{2.5} to PM₁₀ nitrate ratio in Table 3 shows an increase at downtown Los Angeles. This increase is equivalent to an increase in fine ammonium nitrate, and suggests a gradual increase in ammonia availability at this ammonia-limited area. This increase can be explained by an increase in ammonia emissions from motor vehicles. Fraser and Cass (1998) calculated the ammonia emissions emanating from in-use motor vehicles running under rich air-fuel conditions, with three-way catalytic converters. Their calculation shows an increase in motor vehicles ammonia emissions from 2% of Basin-wide total emissions (before the introduction of catalytic converter-equipped vehicles in 1975) to 15% of the inventory, which is almost the same amount of emissions as occur from the most important ammonia source, livestock waste, in the Basin. In an ammonia-limited area, an increase in ammonia emissions leads to an increase in nitrate concentration.

3) A large reduction in NO_x emissions also occurred in the Basin, as shown in Figure 5. A reduction in NO_x emissions results in the reduction of nitric acid. Since the ammonia concentration is sufficient to neutralize nitric acid at Rubidoux (an ammonia-rich area), the resulting nitric acid reduction is directly reflected by a decrease in ammonium and nitrate. However, at an ammonia-limited area such as downtown Los Angeles, nitrate reduction is not observed (despite the large amount of reduction in Basin total NO_x emissions) until the abundant nitric acid level falls to a limited nitric acid level.

A reduction in organic carbon was observed at both sites. Organic carbon is composed of directly emitted primary organic carbon and chemically formed secondary organic carbon. As shown in Figure 5, emission reductions occurred from both crustal and motor vehicle sources that are mainly responsible for the primary organic carbon, and from VOC emissions that are a precursor to the secondary organic carbon; however, these emission reductions alone do not clearly show which one mainly led the reduction in organic carbon. The driver is explained by the PM_{2.5} to PM₁₀ ratio for organic carbon summarized in Table 3, which indicates that the ratio has

decreased at both sites. This suggests that the organic carbon is getting coarser. Thus organic carbon has decreased in the past 19 years, with greater reduction in secondary organic carbon and fine PM_{2.5} organic carbon. Secondary organic carbon is about 15-31% (Schauer et al, 1996) of the total organic carbon on an annual average basis; this fraction may decrease in the future if reduction is maintained at the same rate.

Also as shown in Figure 3, the PM₁₀ EC concentration does not show a significant decrease from 1986 to 1998. There was a slight decrease in EC concentration at downtown Los Angeles, but a slight increase at Rubidoux. However, as previously shown in Figure 4, PM_{2.5} EC shows a significant decrease at Los Angeles and Rubidoux from 1986 to 2005. Major sources of this EC are diesel exhaust, and tire and brake wear. There has been a decrease in diesel exhaust emissions since 1986, as shown in Figure 5. This would result in decreased EC concentration. However, whereas there were relatively small contributions from tire and brake wear in 1986, there has been a subsequent increase due to a continuous increase in the number of motor vehicles (and radial tires) since 1986. One would theorize that the decrease in fine diesel exhaust and the increase in coarse tire and brake wear emissions must balance out for PM₁₀ EC from 1986 to 1998. This can be confirmed in the PM_{2.5} to PM₁₀ ratio summarized in Table 3. As this table indicates, the PM_{2.5} to PM₁₀ ratio of EC decreases at both sites; in other words, the coarse portion of the EC increases. This implies that the EC has become coarser due to the increase in coarse brake and tire wear PM. This increase in coarse EC and decrease in fine EC from diesel exhaust explains why there is almost no change in PM₁₀ EC concentration from 1986 to 1998.

A reduction in crustal component for both PM₁₀ and PM_{2.5} is clearly shown during the period 1986 to 1995 for both sites and it was one of the main components which drove the reduction of PM levels during that period. The fugitive dust rule (SCAQMD Rule 461) developed to control crustal component took effect in 1992 and the enforcement of this rule was directly reflected in the reduction of fugitive crustal concentrations. Crustal concentration slightly increased during the period 1995 to 1998, which might be a result of the population and activity growth in the Basin even while the same dust rule is enforced.

PM_{2.5} to PM₁₀ mass ratios for the downtown Los Angeles and Rubidoux sites, as summarized in Table 3, show an interesting contrast. The

PM_{2.5} to PM₁₀ mass ratio at downtown Los Angeles decreased, while it increased at Rubidoux. This implies that more fine particles were reduced at downtown Los Angeles, resulting in coarser PM₁₀ whereas more coarse particles were reduced at Rubidoux, resulting in finer PM₁₀.

4. SUMMARY AND CONCLUSIONS

Twenty-two years of routine PM₁₀ data and nine years of PM_{2.5} data show that the PM trend is clearly downward in the Basin, reflecting regulatory efforts by the District and other agencies to improve PM air quality. Four years of special monitoring data show that each chemical component has declined at a different rate. During the period 1986-1995, organic carbon, crustal, and sulfate drove the PM reduction for both sites, while ammonium and nitrate drove the PM reduction during the period 1995-1998. Organic carbon and elemental carbon drove the improvement of PM_{2.5} during the period of 1998-2005 at downtown Los Angeles and nitrate, organic carbon, elemental carbon and crustal component drove the improvement at Rubidoux. These data also show that more fine particles were reduced and PM became coarser at downtown Los Angeles, while more coarse particles were reduced and PM became finer at Rubidoux.

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