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TECHNICAL PAPER

Historical trends in the mass and chemical species concentrations of coarse particulate matter in the Los Angeles Basin and relation to sources and air quality regulations

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To assess the impact of past, current and proposed air quality regulations on coarse particulate matter (CPM), the concentrations of CPM mass and its chemical constituents were examined in the Los Angeles Basin from 1986 to 2009 using PM data acquired from peer-reviewed journals and regulatory agency database. PM_{10} mass levels decreased by approximately half from 1988 to 2009 at the three sampling sites examined- located in downtown Los Angeles, Long Beach and Riverside. Annual CPM mass concentrations were calculated from the difference between daily PM_{10} and $PM_{2.5}$ from 1999 to 2009. High CPM episodes driven by high wind speed/stagnant condition caused year-to-year fluctuations in the $99^{th}/98^{th}$ percentile CPM levels. The reductions of average CPM levels were lower than those of PM_{10} in the same period, therefore the decrease of PM_{10} level was mainly driven by reductions in the emission levels of $PM_{2.5}$ (or fine) particles, as demonstrated by the higher annual reduction of average $PM_{2.5}$ (0.92 $\mu g/m^3$) compared with CPM (0.39 $\mu g/m^3$) from 1999 to 2009 in downtown Los Angeles despite their comparable concentrations. This is further confirmed by the significant decrease of Ni, Cr, V, and EC in the coarse fraction after 1995. On the other hand, the levels of several inorganic ions (sulfate, chloride and to a lesser extent nitrate) remained comparable. From 1995 to 2008, levels of Cu, a tracer of brake wear, either remained similar or decreased at a smaller rate compared with elements of combustion origins. This differential reduction of CPM components suggests that past and current regulations may have been more effective in reducing fugitive dust (Al, Fe and Si) and combustion emissions (Ni, Cr, V, and EC) rather than CPM from vehicular abrasion (Cu) and inorganic ions (NO_3^-, SO_4^{2-} and Cl^-) in urban areas.

Implications: Limited information is currently available to provide the scientific basis for understanding the sources and physical and chemical variations of CPM, and their relations to air quality regulations and adverse health effects. This study investigates the historical trends of CPM mass and its chemical components in the Los Angeles Basin to advance our understanding on the impact of past and current air quality regulations on the coarse fraction of PM. The results of this study will aid policy makers to design more targeted regulations to control CPM sources to ensure substantial protection of public health from CPM exposure.

Supplemental Materials: Supplemental materials are available for this article. Go to the publisher's online edition of the *Journal of the Air & Waste Management Association* for (1) details of the sampling sites and (2) the daily concentrations of high CPM/PM_{10} episodes.

Introduction

The U.S. Environmental Protection Agency (EPA) established the National Ambient Air Quality Standards (NAAQS) for ambient particulate matter (PM) to protect human health and public welfare under the jurisdiction of U.S. Clean Air Act. The standard of total suspended particle (TSP) was first introduced in 1971. In 1987, the EPA replaced the TSP standard by the PM_{10} (particles smaller than 10 μm in aerodynamic diameter) standard to control respirable particles. $PM_{2.5}$ (particles smaller than 2.5 μm in aerodynamic diameter) standards were promulgated in 1997 to specifically regulate fine particles that are able to penetrate deeper into the respiratory tract. Currently, coarse particulate matter ($PM_{10-2.5}$, herein referred as CPM) is regulated using PM_{10} standards. However, due to the different sources, and formation/removal mechanisms of fine and coarse particles, the PM_{10} standard may not be an appropriate measure to control the coarse fraction of PM. In contrast to the combustion origins of fine particles in the Los Angeles Basin, CPM is primarily derived from mechanical processes such as grinding and erosion. Major components of CPM include crustal material, sea salt, and biological material, as well as particles of anthropogenic sources such as fugitive and road dust, and secondarily formed ions (Cheung et al., 2011a; Koulouri et al., 2008;

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Sillanpaa et al., 2006; Terzi et al., 2010). In the last decade, a significant body of new research has documented substantive differences of fine and coarse particles, and there is a growing evidence of health effects induced by CPM (Chen et al., 2005; Yeatts et al., 2007). As a result, the need for a new $PM_{10-2.5}$ standard was proposed in a recent review (2006) of NAAQS (U.S. EPA, 2006). The proposed $PM_{10-2.5}$ standard was suggested to be 65–85 $\mu g/m^3$, in the form of a 98th percentile, and it was intended to be generally equivalent to the 1987 24-hr PM_{10} standard (150 $\mu g/m^3$, with a 99th percentile form). Due to the different sources and size distribution of PM in urban and rural areas, the proposed CPM standard would impact these areas differently. Nonetheless, the effects of the proposed standard on industrial and agricultural communities, as well as local regulatory agencies, are largely unknown.

The study described here examines the trend of CPM mass concentration and chemical composition in the Los Angeles Basin over the past two decades, as well as the implications of the proposed $PM_{10-2.5}$ standard given the nature and sources of PM components in the basin. The Los Angeles Basin is located in Southern California, and is the second most populous metropolitan area in the United States. The basin is served by the nation's largest port complex, a large freight and passenger rail infrastructure, numerous airports, and an extensive network of freeways and highways. Due to its local topography and meteorological conditions, heavy reliance on vehicles and traffic activity from the ports, Los Angeles is ranked among the worst cities for ozone and particulate pollution (American Lung Association, 2011), and has been an area of active air quality research. Studies examining characteristics of ambient aerosols across the basin have been conducted since the 1940s (Neiburger and Wurtele, 1949), and a large body of historical PM data is available from regulatory agencies and academic institutes. Additionally, the contribution of coarse particle to PM_{10} is relatively high (on average 33–58%) in Los Angeles (Gauderman et al., 2000; Pakbin et al., 2010) compared with several other large US metropolitan areas (2004), thereby making it feasible to study coarse particle trends/composition with lower uncertainty. All of these provide a unique opportunity to examine the historical trends of coarse particle in this basin, which will allow us to assess how the CPM fraction has been impacted by past and current air quality regulations, as well as implications of the proposed standards.

Methodology

To study the CPM trend in the Los Angeles Basin, three representative areas (downtown Los Angeles, Long Beach, and Riverside) were selected based on the availability of historical data sets. Figure 1 shows a map of the sampling sites in the three regions. Geographical coordinates of sampling sites are provided in Table S1 in the supplemental materials. Downtown Los Angeles (sites DLA and USC) is a typical urban area with high commercial and traffic activity. The downtown area is characterized by dense freeway networks and a high volume of both heavy- and light-duty vehicles. DLA is a monitoring site maintained by the South Coast Air Quality Management District (SCAQMD) and is located within 900 m of freeways I-5 and I-110. The other site in Los Angeles (USC) is located about 150 m east of I-110. Long Beach (sites HUD, NLB, LBCC, and S3) is a mixed residential and commercial neighborhood. The sampling sites in Long Beach are in close vicinity to the Port of Los Angeles and Port of Long Beach, and are highly influenced by heavy-duty diesel vehicle traffic related to harbor activity. NLB and HUD are maintained by the SCAQMD. NLB is located approximately 600 m north of I-405 and 1.2 km east of I-710. HUD is about 100 m east of Terminal Island Freeway and 1.2 km west of I-710. LBCC is located at the campus of Long Beach City College approximately 2.5 km north of I-405. The S3 site was one of the sampling sites in a study that examined

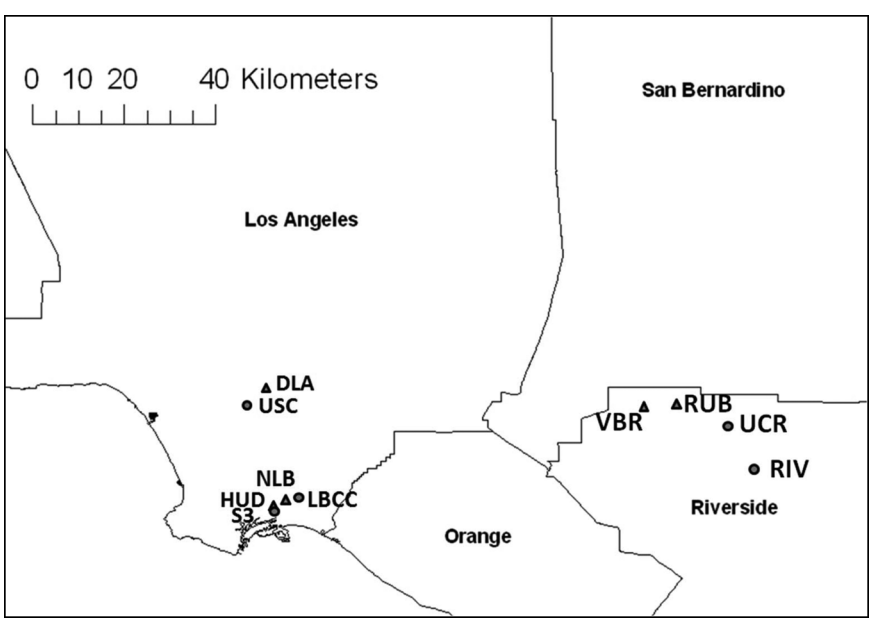

Figure 1. Map of the samplings sites in downtown Los Angeles (DLA and USC), Long Beach (NLB, HUD, LBCC, and S3), and Riverside (RUB, VBR, UCR, and RIV). Sites operated and maintained by the SCAQMD are represented in triangles.

size-segregated PM in communities of the Los Angeles Harbor (Arhami et al., 2009), and it is about 900 m south of the HUD site. Riverside (sites VBR, RUB, UCR, and RIV) is a suburban area located 80 km inland and downwind of Los Angeles, and is generally considered to be a receptor site for pollutants generated in urban Los Angeles and advected to the area within a few hours after their emissions. VBR and RUB are SCAQMD monitoring sites located about 2.5 km and 800 m south of CA-60, respectively. The UCR site is situated at the Citrus Research Center and Agricultural Experiment Station of the University of California, Riverside, and it is upwind of surrounding freeways. RIV is located at a retirement home that is 15 km southeast of downtown Riverside.

The CPM mass concentration data presented in Figures 2–4 were calculated as the difference between PM_{10} and $PM_{2.5}$ levels (the subtraction method). Daily PM_{10} and $PM_{2.5}$ measurements were obtained from the online database of California Air Resources Board (CARB). The three sampling sites (DLA, NLB, and RUB) used in this analysis were maintained by SCAQMD, and the details of the sampling methods are described under Title 40 Part 58 of Code of Federal Regulations. In brief, daily $PM_{2.5}$ measurements were quantified gravimetrically using sequential samplers operating at 16.7 L/min (Andersen Model Reference Ambient Air Sampler 2.5-300; Andersen Instruments Inc., Smyrna, GA), loaded with a 2-μm Teflon substrate. PM_{10} measurements were determined gravimetrically using high-volume samplers (Sierra Andersen/General Metal Works Model 1200; Sierra Andersen, Smyrna, GA, and General Metal Works, Cleves, OH) loaded with a quartz microfiber filter. Daily PM_{10} concentrations from 1988 to 2009 were analyzed. $PM_{2.5}$ measurements were only available after 1999, and daily CPM mass concentrations were calculated from 1999 to 2009 using the subtraction method when both measurements were available for the same day. Note that the reported mass concentrations were collected using samplers with no denuders. The distinct flow rates used in the PM_{10} and $PM_{2.5}$ samplers might contribute to the differential loss of semivolatile compounds, in additional to other sampling artifacts that could be different in the two samplers. Since the majority of semivolatile compounds resides in the fine PM fraction (Miguel et al., 2004; Yoshizumi and Hoshi, 1985), the estimation of CPM using the subtraction method (calculated based on reported concentrations from the low-volume-$PM_{2.5}$ sampler and the high-volume-PM_{10} sampler) might have underestimated the mass concentrations of coarse particles. Nonetheless, the sampling artifacts of semivolatile organics are likely to be reduced by the long sampling

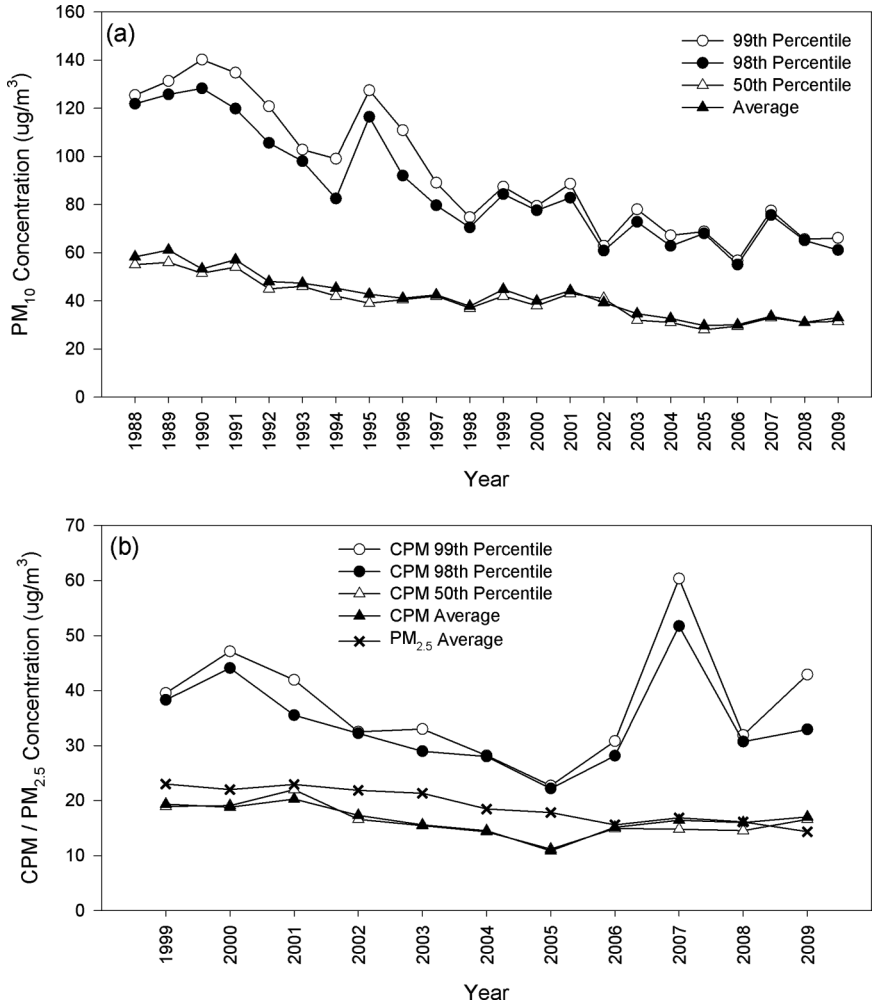

Figure 2. Annual concentrations of (a) PM_{10} from 1988 to 2009 and (b) CPM/$PM_{2.5}$ from 1999 to 2009 in downtown Los Angeles.

time (24 hr) and higher mass loadings (Sardar et al., 2005; Mader et al., 2003). On the other hand, due to the stronger removal process of CPM compared with fine PM, coarse particles could be more spatially heterogeneous (Pakbin et al., 2010), and the extrapolation of this analysis to other air basins needs to be proceeded with cautions. Daily PM_{10} levels were generally measured once every 6 days, with an average yearly count of 59 ± 3.5, 85 ± 27, and 57.8 ± 3.4 from 1988 to 2009 in downtown Los Angeles, Riverside, and Long Beach, respectively. The higher number count in Riverside was driven by the more frequent measurements (once every 3 days) from 2000 to 2009. $PM_{2.5}$ was measured more frequently, with an average annual measurement count of 305 ± 58, 308 ± 56, and 303 ± 60 from 1999 to 2009 in DLA, RUB, and NLB, respectively. The higher standard deviation was driven by the lower count in year 1999 when the measurements first started.

Concentrations of CPM mass and chemical constituents presented in Figures 5–7 were obtained from studies fully or in part published in the peer-reviewed literature before 2010. Although a number of studies have examined the chemical composition of ambient PM in Los Angeles, very few of them report data for coarse particles (or allow the calculation of such). Seven studies, providing chemical speciation of elemental species, were included in our analyses. The earliest study that performed chemical speciation on both PM_{10} and $PM_{2.5}$ in the Los Angeles Basin was conducted in 1986. The year-long data set was available at CARB (Solomon et al., 1988), and part of the PM data were published in peer-reviewed literature (Eldering et al., 1991; Solomon et al., 1989, 1992). Shortly after, Chow et al. (1994) conducted an intensive study in 1987 to capture photochemical episodes in warmer periods (June to September) and stagnation episodes in cooler periods (November to December). A more comprehensive project was carried out by the SCAQMD from January 1995 to February 1996 to investigate the chemical composition of ambient PM_{10} and $PM_{2.5}$ in an effort to better characterize emission inventories and improve performance of modeling tools (Kim et al., 2000a, 2000b). From 2000 to 2009, a few additional studies were conducted in Los Angeles, Long Beach, and Riverside to examine the chemical composition of size-fractionated airborne PM to advance the understanding of the sources, atmospheric processing of ambient particles, and their human health impacts (Arhami et al., 2009; Polidori et al., 2009; Sardar et al., 2005). In 2008, a comprehensive investigation on ambient CPM was conducted to study the chemical mass closure, as well as the spatial and temporal variations of CPM in the Los Angeles Basin (Cheung et al., 2011a, 2011b; Moore et al., 2010; Pakbin et al., 2010, 2011). Table 1 summarizes the sampling location, sampling time and frequency, sampling instrument and method, analytical method, and other background information of each study. CPM concentrations were obtained using the difference between reported PM_{10} and $PM_{2.5}$ levels in the three earlier studies (Chow et al., 1994; Kim et al., 2000a; Solomon et al., 1988). The more recent studies employed samplers segregating particles by size, and CPM concentrations and chemical composition were obtained directly as measured in the coarse fraction (Arhami et al., 2009; Cheung et al., 2011a; Polidori et al., 2009; Sardar et al., 2005).

Results and Discussion

Trends in CPM mass concentrations

Table 2a–c shows selected meteorological parameters at the downtown Los Angeles (DLA), Long Beach (NLB), and Riverside (RUB) sampling sites, respectively. This information was acquired from the online database of CARB; only data after 1994 were available at the three sampling sites. The annual averages of temperature and relative humidity were calculated based on hourly data. Overall, annual average temperatures were consistent (average = 17.9 °C, standard deviation = 0.81 °C) from 1994 to 2009, whereas higher year-to-year fluctuations (average = 59.3%, standard deviation = 11%) were observed for the relative humidity (RH). In general, the annual average temperature and relative humidity was similar in Los Angeles and Long Beach. Riverside's inland location was highlighted by the higher average temperature and standard deviation, coupled with the lower relative humidity. Wind originating from the west dominated most of the year, in accordance with the typical onshore flow patterns in the Los Angeles Basin. The prevailing westerly onshore wind from the Pacific Ocean started in late morning and remained strong until evening. At night, wind direction reversed and the northerly/northeasterly wind prevailed. The wind speed was generally lower overnight. Overall, large-scale meteorological conditions were relatively consistent in this basin, and did not appear to influence the observed PM trends, as discussed and presented below.

In downtown Los Angeles, the 99th percentile for PM_{10} (Figure 2a) and CPM (Figure 2b) ranges from 56.7 to 88.6 $\mu g/m^3$ and from 22.7 to 60.4 $\mu g/m^3$, respectively, from 1999 to 2009. The spike in the 99th and 98th percentiles in 2007 was driven by 2 days of high CPM concentrations (69 and 51 $\mu g/m^3$ in April and October, respectively), as shown in Figure S1 in supplemental materials. The PM_{10} level was in attainment of the federal 24-hr standard (150 $\mu g/m^3$) but in violation of the California standard (50 $\mu g/m^3$) throughout the entire study period. Since the current PM_{10} standard is expressed in the 99th percentile form and the proposed CPM standard is set in the 98th percentile form, their comparability is examined. The difference between the 99th and 98th percentiles is more apparent in the early 1990s, with insignificant difference after 1998. The average and median PM_{10} concentrations agree fairly well. The slope of the 99th percentile concentration is 3.71 $\mu g/m^3$, with a R^2 of 0.82 (Table 3a), indicating an average annual decrease of 3.71 $\mu g/m^3$ of the 99th percentile PM_{10} mass concentration from 1988 to 2009. The corresponding reduction is 1.33 $\mu g/m^3$ for the average PM_{10} concentration. CPM levels did not exhibit the typically consistent decreasing trend observed in the PM_{10} data. The slope of the average CPM concentration is −0.39 $\mu g/m^3$ ($P = 0.11$) from 1999 to 2009 (corresponding slopes are −1.33 $\mu g/m^3$ and −0.92 $\mu g/m^3$ for PM_{10} and $PM_{2.5}$, respectively, both with a P value of less than 0.001), indicating that the reduction of PM_{10} is mostly driven by the decrease of $PM_{2.5}$ given the comparable levels of fine and coarse PM (average annual fine-to-coarse ratio = 1.18 ± 0.21 from 1999 to 2009). To investigate the degree of equivalency between the current PM_{10} and the proposed $PM_{10-2.5}$ standards, the number of exceedances was

Table 1. Samping location, sampling time and frequency, sampling instrument and method, analytical method, and other background information of the seven studies analyzed

	1986, CARB	Chow et al., 1994	Kim et al., 2000a	Sardar et al., 2005	Polidori et al., 2009	Arhami et al., 2009	Cheung et al., 2011
Location	AQMD Los Angeles (DLA) AQMD Rubidoux (RUB) AQMD Long Beach (NLB)	AQMD Los Angeles (DLA) AQMD Rubidoux (RUB) Long Beach City College (LBCC)	AQMD Los Angeles (DLA) AQMD Rubidoux (RUB)	USC in Los Angeles UCR in Riverside	Riverside retirement home (RIV)	S3in Long Beach	USC in Los Angeles AQMD Van Buren (VBR) AQMD Long Beach (HUD)
Sampling period	Jan–Dec 1986	11 days in Jun–Sep, 6 days in Nov–Dec in 1987	Jan 1995–Feb 1996	USC: Oct 2002–Sep 2003; UCR: Mar–Jun 2001	Aug–Oct 2006, Jan–Feb 2007	Mar–May 2007	Apr 2008–Mar 2009
Sampling time	Once every 6th day, daily samples	Sequential samples for each episode (5 in summer, 3 in winter)	Once every 3rd or 6th day, daily samples	Once every week, daily samples	7 weekly samples	6 weekly samples	Once every week, daily samples on Wednesday
Filter type	PTFE and quartz	Teflon and quartz	Teflon and quartz	Teflon and aluminum	Zefluor	Zefluor and quartz	Zefluor and quart
Sampling method	PM_{10}: 16.7 lpm through a PM_{10} inlet, 5.6 lpm through each filter $PM_{2.2}$: 24.8 lpm to a cuclone separator with a cut point of 2.2 μm; 3–4.6 lpm through each filter	PM_{10}: 110 lpm through a PM_{10} inlet, 30 lpm through each filter $PM_{2.5}$: 110 lpm to a cyclone separator with a cut point of 2.5 μm; 35 lpm through each filter	PM_{10}: 97 lpm through a PM_{10} inlet, 10 lpm through each filterPM2.2 $PM_{2.5}$: 112 lpm to a cyclone separator with a cut point of 2.5 μm; 20 lpm through each filter	Micro-Orifice Uniform Deposition Impactor (MOUDI) operated at 30 lpm; Partisol sampler with PM_{10} and $PM_{2.5}$ inlets operated at 16.7 lpm	Personal Cascade Impactor Sampler (PCIS) operated at 9 lpm with a PM_{10} inlet	PCIS operated at 9 lpm with a PM_{10} inlet	USC Virtual Impactor (VI) operated at a total flow of 50 lpm and a minor flow of 2 lpm with a PM_{10} inlet; PCIS operated at 9 lpm with a PM_{10} inlet
Analytic method (For elements, ions, and carboneous contents)	X-ray fluorescence Ion chromatography. Thermal desorption/ optical transmission	X-ray fluorescence Ion chromatography. Automated colorimetry, atomic absorption Thermal manganese oxidation	X-ray fluorescence Ion chromatography Optical thermal carbon analyzer	X-ray fluorescence Ion chromatography Thermal disorption/ optical transmission	ICP-MS NA Thermal disorption/ optical transmission	ICP-MS Ion chromatography NA	ICP-MS Ion chromatography Thermal disorption/ optical transmission
CPM calculation	Indirect, difference between PM_{10} and $PM_{2.5}$	Indirect, difference between PM_{10} and $PM_{2.5}$	Indirect, difference between PM_{10} and $PM_{2.5}$	Direct	Direct	Direct	Direct
Statistics	Average	Average	Average	Average	Average	NA, composites	Average

Table 2. Selected meteorological parameters from 1994 to 2009 in (a) downtown Los Angeles, (b) Long Beach, and (c) Riverside

	Temperature		Relative Humidity		Dominant Wind	
	Avg. (°C)	SD	Avg. (%)	SD	Direction (%)	Speed (mps)
(a) Downtown Los Angeles						
1994	17.5	5.7	53.0	16.1	NA	
1995	17.7	5.1	57.1	15.9	W (19.2%)	2.6
1996	18.0	5.3	55.3	15.8	W (19.2%)	2.8
1997	NA		46.3	13.4	W (16.3%)	2.9
1998	NA		NA		NA	
1999	17.3	5.3	51.4	15.2	W (21.0%)	3.0
2000	18.1	5.4	51.0	16.2	NA	
2001	17.7	6.3	64.9	17.7	W (23.0%)	2.8
2002	17.8	6.0	60.3	18.8	NE (21.2), W (21.2%)	1.9 / 2.8
2003	16.4	5.3	59.0	20.1	NA	
2004	18.3	5.9	60.9	18.9	S (19.4%), W (19.1%)	2.5 / 3.6
2005	18.2	5.5	53.8	25.7	NE (20.2%)	2.3
2006	18.4	6.3	61.7	18.6	NA	
2007	18.1	6.3	60.5	19.3	W (22.0%)	2.7
2008	18.5	6.5	60.2	19.4	W (23.4%)	2.7
2009	18.4	6.2	59.3	18.8	W (27.9%)	3.1

	Temperature		Relative Humidity		Dominant Wind	
	Avg. (°C)	SD	Avg. (%)	SD	Direction (%)	Speed (mps)
(b) Long Beach						
1994	17.1	4.9	52.0	13	NA	
1995	17.1	4.3	58.3	14	W (23.4%)	2.1
1996	16.0	5.7	45.1	20	W (22.4%)	2.2
1997	NA		69.1	22	W (20.9%)	2.0
1998	17.7	5.1	68.5	27	NA	
1999	16.8	4.9	59.8	27	W (27.8%)	2.0
2000	17.6	4.9	72.5	21	NA	
2001	16.8	4.8	72.5	17	W (24.9%)	1.8
2002	17.1	4.7	70.6	18	W (21.9%)	1.8
2003	17.8	4.9	64.2	29	W (20.7%)	1.8
2004	17.4	4.9	70.2	22	W (26.2%)	2.2
2005	17.5	4.6	71.4	24	W (29.2%)	2.3
2006	17.7	5.4	70.2	24	NA	
2007	17.3	5.2	67.8	25	W (30.5%)	2.3
2008	17.7	5.5	69.1	25	W (31.5%)	2.2
2009	17.1	5.2	68.6	25	W (28.7%)	2.3

	Temperature		Relative Humidity		Dominant Wind	
	Avg. (°C)	SD	Avg. (%)	SD	Direction (%)	Speed (mps)
(c) Riverside						
1994	17.7	7.3	48.9	18	NA	
1995	18.1	7.1	48.2	17	W (22.7%)	1.7
1996	18.4	7.2	48.4	19	W (26.4%)	1.9
1997	NA		69.1	22	NA	
1998	19.9	8.1	NA		NA	
1999	18.1	7.6	44.3	30	NW (24.1%)	2.3
2000	18.7	7.5	60.8	26	NA	
2001	18.3	7.8	64.3	25	W (30.6%)	2.5
2002	18.3	7.4	63.4	27	W (27.2%)	2.4
2003	18.9	7.8	61.1	28	W (24.5%)	2.3
2004	18.7	7.4	60.0	25	NW (22.4%)	2.3
2005	18.8	7.0	67.8	27	NW (25.5%)	2.2
2006	19.1	7.9	63.6	28	NA	
2007	19.0	7.8	61.6	28	NW (26.4%)	2.3
2008	19.5	8.1	62.2	27	NW (26.8%)	2.3
2009	19.1	7.7	59.6	27	W (24.0%)	2.4

Table 3. Linear regression analysis of PM data (PM_{10} from 1988 to 2009, $PM_{10\text{-}2.5}$ and $PM_{2.5}$ from 1999 to 2009) in (a) downtown Los Angeles, (b) Long Beach, and (c) Riverside

		Linear Regression	R^2	**P**
(a) Downtown Los Angeles				
PM_{10}	99th percentile	$y = -3.71\ (\pm 0.39)\ x + 136\ (\pm 5.2)$	0.82	<0.001
	98th percentile	$y = -3.21\ (\pm 0.36)\ x + 124\ (\pm 4.8)$	0.80	<0.001
	50th percentile	$y = -1.19\ (\pm 0.12)\ x + 54.0\ (\pm 1.6)$	0.83	<0.001
	Average	$y = -1.33\ (\pm 0.12)\ x + 57.4\ (\pm 1.6)$	0.86	<0.001
$PM_{10\text{-}2.5}$	99th percentile	$y = -0.02\ (\pm 1.1)\ x + 37.5\ (\pm 7.1)$	0.00	0.98
	98th percentile	$y = -0.42\ (\pm 0.82)\ x + 36.4\ (\pm 5.6)$	0.03	0.62
	50th percentile	$y = -0.54\ (\pm 0.23)\ x + 19.5\ (\pm 1.6)$	0.37	0.05
	Average	$y = -0.39\ (\pm 0.23)\ x + 18.9\ (\pm 1.5)$	0.25	0.11
$PM_{2.5}$	Average	$y = -0.92\ (\pm 0.09)\ x + 24.6\ (\pm 0.64)$	0.91	<0.001
		Linear Regression	R^2	**P**
(b) Long Beach				
PM_{10}	99th percentile	$y = -2.60\ (\pm 0.64)\ x + 110\ (\pm 8.1)$	0.46	<0.001
	98th percentile	$y = -2.46\ (\pm 0.60)\ x + 103\ (\pm 7.5)$	0.47	<0.001
	50th percentile	$y = -0.62\ (\pm 0.11)\ x + 40.5\ (\pm 1.3)$	0.64	<0.001
	Average	$y = -0.76\ (\pm 0.11)\ x + 44.8\ (\pm 1.4)$	0.72	<0.001
$PM_{10\text{-}2.5}$	99th percentile	$y = -0.50\ (\pm 0.69)\ x + 41.0\ (\pm 4.7)$	0.06	0.48
	98th percentile	$y = -0.59\ (\pm 0.30)\ x + 34.9\ (\pm 2.0)$	0.31	0.08
	50th percentile	$y = -0.37\ (\pm 0.14)\ x + 17.1\ (\pm 0.96)$	0.43	0.03
	Average	$y = -0.22\ (\pm 0.11)\ x + 17.0\ (\pm 0.74)$	0.31	0.07
$PM_{2.5}$	Average	$y = -0.87\ (\pm 0.09)\ x + 22.4\ (\pm 0.61)$	0.91	<0.001
		Linear Regression	R^2	**P**
(c) Riverside				
PM_{10}	99th percentile	$y = -5.38\ (\pm 0.85)\ x + 207\ (\pm 11)$	0.67	<0.001
	98th percentile	$y = -4.72\ (\pm 0.77)\ x + 189\ (\pm 10)$	0.65	<0.001
	50th percentile	$y = -1.59\ (\pm 0.21)\ x + 82.2\ (\pm 2.8)$	0.74	<0.001
	Average	$y = -1.76\ (\pm 0.23)\ x + 84.6\ (\pm 3.0)$	0.75	<0.001
$PM_{10\text{-}2.5}$	99th percentile	$y = -2.36\ (\pm 1.1)\ x + 93.8\ (\pm 7.7)$	0.32	0.07
	98th percentile	$y = -1.77\ (\pm 0.98)\ x + 84.2\ (\pm 6.7)$	0.27	0.11
	50th percentile	$y = -0.56\ (\pm 0.37)\ x + 35.2\ (\pm 2.5)$	0.21	0.16
	Average	$y = -0.57\ (\pm 0.29)\ x + 35.7\ (\pm 2.0)$	0.30	0.08
$PM_{2.5}$	Average	$y = -1.69\ (\pm 0.12)\ x + 33.5\ (\pm 0.84)$	0.96	<0.001

Notes: Values in parentheses represent standard errors of the slope and intercept.

examined using the 99th percentile of PM_{10} level and the 98th percentile of the CPM level from 1999 to 2009. In both cases, zero violations were observed. For further comparisons of the two standards, the ratio of the annual PM level to the corresponding standards (i.e., calculated as the annual 99th percentile PM_{10} to 150 $\mu g/m^3$ for the PM_{10} standard and the annual 98th percentile CPM to 70 $\mu g/m^3$ for the CPM standard) was examined. Using the data from 1999 to 2009, the ratios for the current PM_{10} and proposed $PM_{10\text{–}2.5}$ standards were 0.48 ± 0.12 and 0.48 ± 0.07, respectively, suggesting that the two standards are comparable in downtown Los Angeles.

In Long Beach, the 99th percentile PM_{10} level experienced a fluctuating decreasing trend with a R^2 of 0.46, as shown in Figure 3a. The spike in 1995 was driven by an episode of high PM_{10} level from mid-November to early December, as illustrated in Figure S2. The wind speed during that period was relatively low with more than 70% of the time with "calm" conditions (wind speed less than 0.5 m/sec). It is possible that the high PM_{10} levels were due to the low dispersion of the emissions generated from the nearby harbor activity. The 99th percentile PM_{10} level ranges from 52.5 to 143.1 $\mu g/m^3$ from 1988 to 2009, attaining the EPA standard but violating the California standard. The decreasing trend of the average PM_{10} levels exhibits a high R^2 of 0.72 from 1988 to 2009 (Figure 3a and Table 3b). However, the average PM_{10} reduction rate is lower in the last 5 years, as evident by the lower slope of -0.14 $\mu g/m^3$ (standard error = 0.25 $\mu g/m^3$) from 2005 to 2009. Similarly, the average CPM concentration was not significantly reduced from 1999 to 2009, as demonstrated by the close to zero slope ($m = -0.22$ $\mu g/m^3$, $P = 0.07$) in Table 3b, in contrast to the significant reduction in

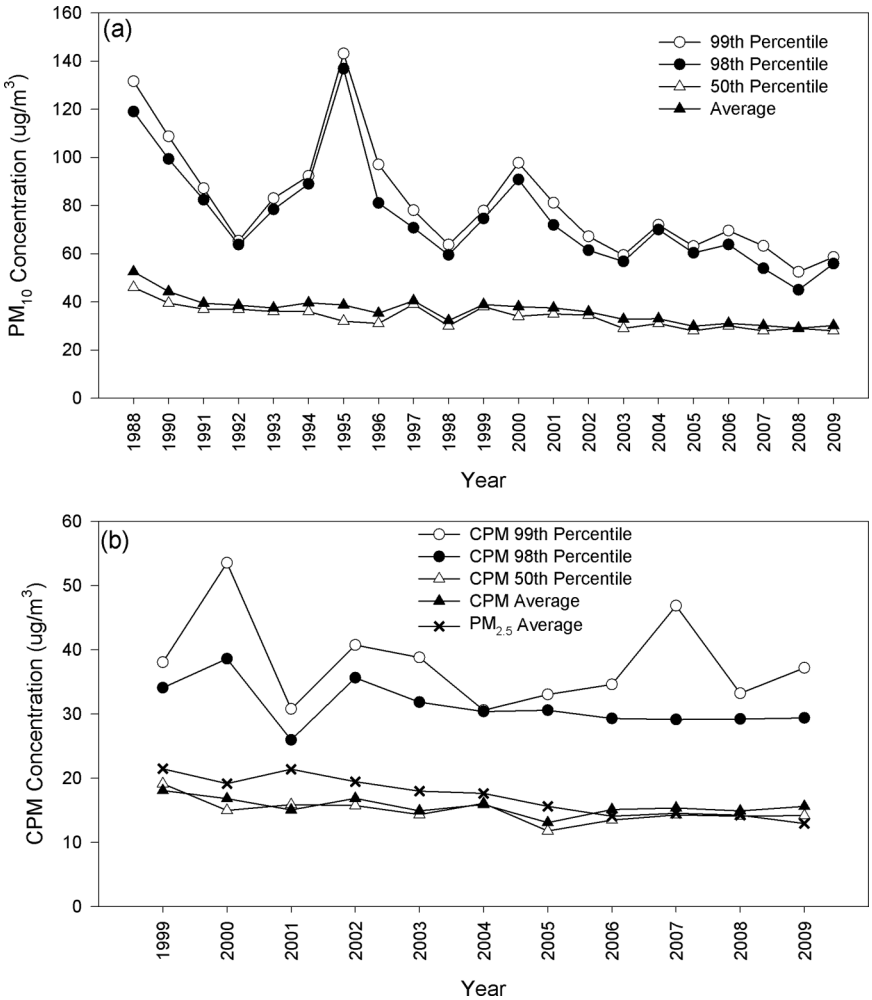

Figure 3. Annual concentrations of (a) PM_{10} from 1988 to 2009 and (b) CPM/$PM_{2.5}$ from 1999 to 2009 in Long Beach.

$PM_{2.5}$ levels ($m = -0.87$ μg/m^3, $P < 0.001$). The sampling site in Long Beach is heavily impacted by the Port's traffic activity. In addition to particle resuspension by wind, CPM is also re--entrained into the atmosphere by traffic-induced turbulence (Pakbin et al., 2010). Heavy-duty vehicles generally induce higher roadway resuspension than light-duty vehicles (Charron and Harrison, 2005). Therefore, it is likely that the effort of PM reduction has been counterbalanced by the increase in the number of heavy-duty vehicles resulted by the expansion and increasing activity of the Los Angeles ports, as the container volume grew from 1 million in 1985 to 7.8 million in 2010 at the Port of Los Angeles. In Long Beach, none of the recorded PM_{10} and calculated CPM levels violated the current federal PM_{10} and proposed CPM standards. The ratios of the 99th percentile PM_{10} and 98th percentile CPM to the current PM_{10} and proposed $PM_{10-2.5}$ standards were 0.46 ± 0.08 and 0.45 ± 0.05, respectively, again demonstrating that the two standards are comparable in Long Beach.

Due to its downwind receptor location and suburban nature, PM_{10}/CPM mass concentrations in Riverside were higher than those observed in Los Angeles. The 99th percentile PM_{10} concentration (Figure 4a) was higher than the federal 24-hr standard of 150 μg/m^3 in 1988–1991, 1993–1995, and 2003, and experienced a moderately fluctuating downward trend from 1988 to 2009 ($R^2 = 0.67$; Table 3c). This is probably due to the suburban nature of the area, where high level of PM_{10} is mostly driven by particle resuspension in episodes of high wind speed (Cheung et al., 2011a; Pakbin et al., 2010). As shown in Table 3c, the average PM_{10} level experienced a more consistent reduction with a R^2 of 0.75. From 1999 to 2009, the reduction of average PM_{10} was largely driven by the decrease in fine PM concentrations ($m = -1.69$ μg/m^3, $P < 0.001$), with a minor contribution from CPM ($m = -0.57$ μg/m^3, $P = 0.08$). The slopes of the 99th percentile and average PM_{10} concentrations are −5.38 and −1.76 μg/m^3, respectively, from 1988 to 2009. The reduction of CPM mass concentration is significantly lower than that observed in the PM_{10} (Figure 4b and Table 3c), and the trend is more variable, although, overall, a decreasing trend is seen as evident by the negative slopes of −2.36 and −0.57 for the 99th percentile and average CPM levels, respectively. The relatively low coefficient of determination in the 99th percentile ($R^2 = 0.32$) is driven by the spike in 2003, due to a week of high CPM levels in October (91.0, 96.3, and 111 μg/m^3 on October 21, 24, and 27, respectively). In Riverside, where the contribution of coarse particles to PM_{10} is generally higher than in Los Angeles and Long Beach due to the high levels of crustal

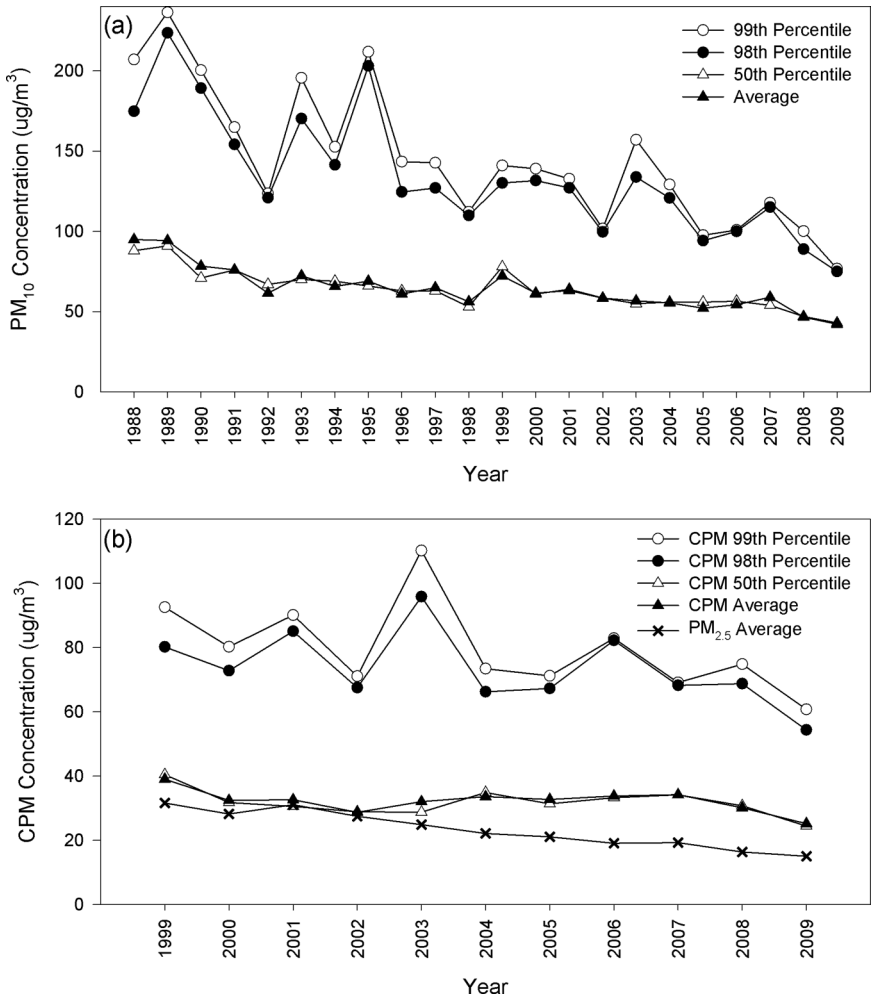

Figure 4. Annual concentrations of (a) PM_{10} from 1988 to 2009 and (b) CPM/$PM_{2.5}$ from 1999 to 2009 in Riverside.

materials in the suburban area (Cheung et al., 2011a), the proposed $PM_{10-2.5}$ standard was not equivalent with the current PM_{10} standard. Using the data from 1999 to 2009, the annual 99th percentile PM_{10} level was higher than the current PM_{10} standard of 150 $\mu g/m^3$ only in 2003. However, the annual 98th percentile CPM level was higher than the proposed CPM standard of 70 $\mu g/m^3$ 5 times (1999–2001, 2003, and 2006) from 1999 to 2009, suggesting that the proposed standard is more stringent than the existing standard in areas dominated by coarse particles, and that Riverside could be in frequent violations with the proposed $PM_{10-2.5}$ standard.

Trends in chemical CPM components

Whereas CPM mass concentrations provide a metric of the overall mass reduction of coarse particles, the examination of CPM chemical composition provides insights on changes in the contribution of different sources to coarse particles, and may thus assist regulatory agencies in the design and implementation of more effective air quality strategies to protect public health. Figures 5–7 present concentrations of CPM chemical constituents, including organic and elemental carbon, elements, and inorganic ions in downtown Los Angeles, Long Beach and Riverside, respectively. Note that the analyses described below focused on the study conducted in 1986 (Solomon et al., 1988), 1995–1996 (Kim et al., 2000b), and 2008–2009 (Cheung et al., 2011a), all of which compiled comprehensive CPM data sets of 1 year or more, and their results are presented as bar charts in Figures 5–7. Although sampling of the three year-long studies was conducted not daily, but rather once every 3rd, 6th, or 7th day, the long sampling period was likely to diminish the impact of temporal variation, and could therefore provide a more representative characterization of CPM. Other studies that were conducted in shorter time frames/smaller spatial scales were shown as line plots, and their results were likely to be influenced by seasonal variations of ambient CPM. Studies conducted before and after 1995 are represented by black and open symbols, respectively.

Mineral dust

Many studies have shown that mineral and road dust are major components of CPM, contributing to 22–65% of CPM mass concentrations in studies conducted in Los Angeles, Athens, Helsinki, Amsterdam, and Eastern Mediterranean (Cheung et al., 2011a; Koulouri et al., 2008; Sillanpaa et al.,

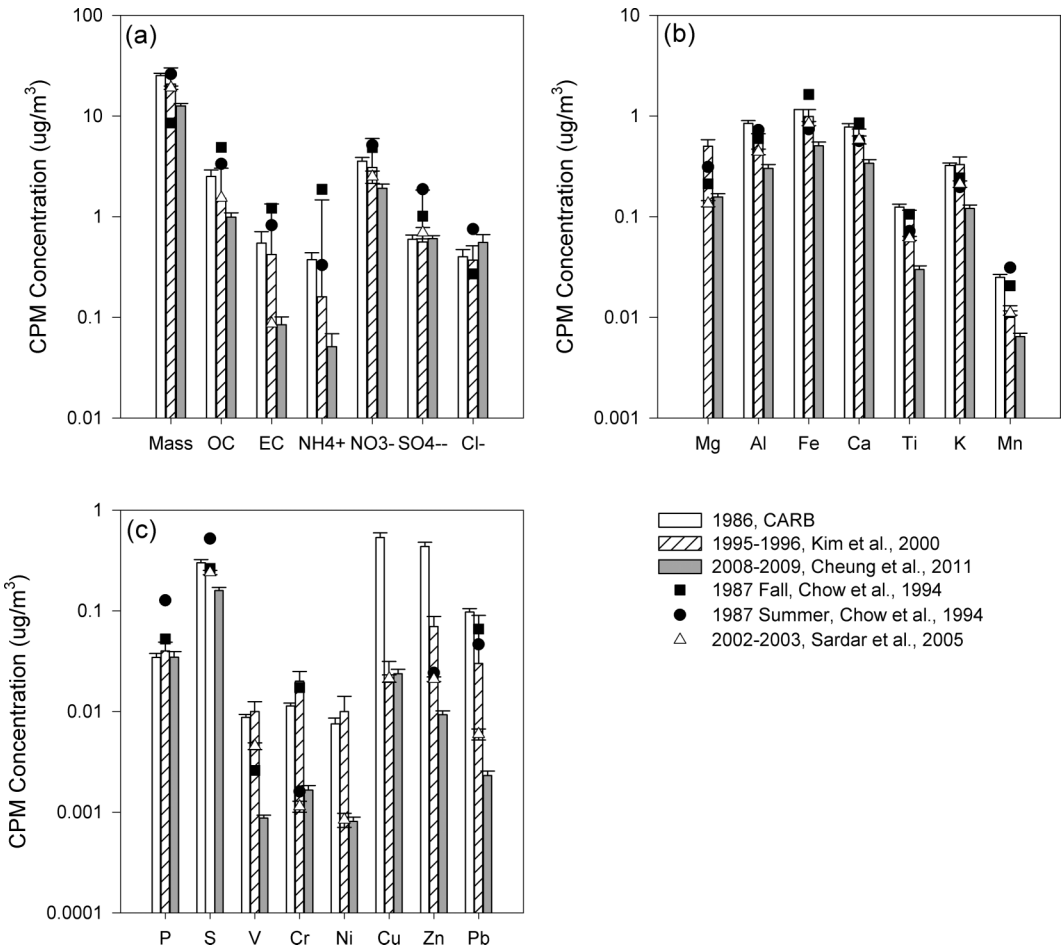

Figure 5. CPM concentrations of (a) mass, organic, and elemental carbon, and inorganic ions; (b) elements of crustal origins; and (c) elements of anthropogenic origins in downtown Los Angeles. Error bars show standard errors of the average when available.

2006). Mineral dust comprises largely of eroded soil particles that have been mobilized and resuspended into the atmosphere by wind and anthropogenic activities. Industrial activities, such as construction and cement plant operations, may contribute to the emission and resuspension of dust. Si, Al, and Fe are the three most abundant major elements in the upper continental crust (Usher et al., 2003) and thereby may serve as tracers of mineral dust (Lough et al., 2005; Pakbin et al., 2011). It should be noted that although Fe in the coarse fraction arises predominantly from crustal materials, it could be enriched from anthropogenic sources such as brake wear in urban areas (Garg et al., 2000). Other crustal-dominated elements include Na, Ca, Ti, K, Mn, and Mg, and their abundances vary depending on location and rock type. The decreasing trends of crustal materials were very consistent in the last two decades. From 1986 to 1995, levels of coarse particulate Al, Fe, and Ti decreased by 34%, 15%, and 20%, respectively, in downtown Los Angeles. Further reductions were observed from 1995 to 2008, when Al, Fe, and Ti concentrations were reduced by 46%, 49%, and 70%, respectively. Such reduction trends were reinforced by the data from Sardar et al. (2005), where sampling was conducted from 2002 to 2003 and the average concentrations of Al, Fe, and Ti stayed between those from Kim et al. (2000a) and Cheung et al. (2011a) The contribution of crustal materials and trace elements to CPM mass were higher in Riverside (54.7%) compared with Los Angeles (42.6%) (Cheung et al., 2011a). In Riverside, CPM Al and Ti concentrations were reduced by 19% and 25%, respectively, from 1986 to 1995, where the corresponding reductions were 70% and 76% from 1995 to 2008. In 1986, the SCAQMD implemented Rule 1112.1 to limit PM emissions from cement kilns. Rule 1186 was adopted in 1997 to reduce the re-entrainment of fugitive dust of PM_{10} emissions from paved and unpaved roads as well as livestock operations. This rule requires owners and operators of paved public roads to remove visible roadway accumulations within 72 hr of notifications. It also requires the paving or stabilization of heavily used unpaved public roads or the reduction of vehicular speed on such roads. In 2005, Rule 1157 was introduced to control PM_{10} emissions from aggregate and related operations by reducing various dust sources from loading, unloading, and transferring activities, process equipment, paved and unpaved roads inside the facilities, etc. The use of dust suppressants or other control methods is required during transfer and loading activities. The observed high reductions of mineral dust could be due to the effectiveness of these regulations in reducing the sources and levels of resuspension of dust particles.

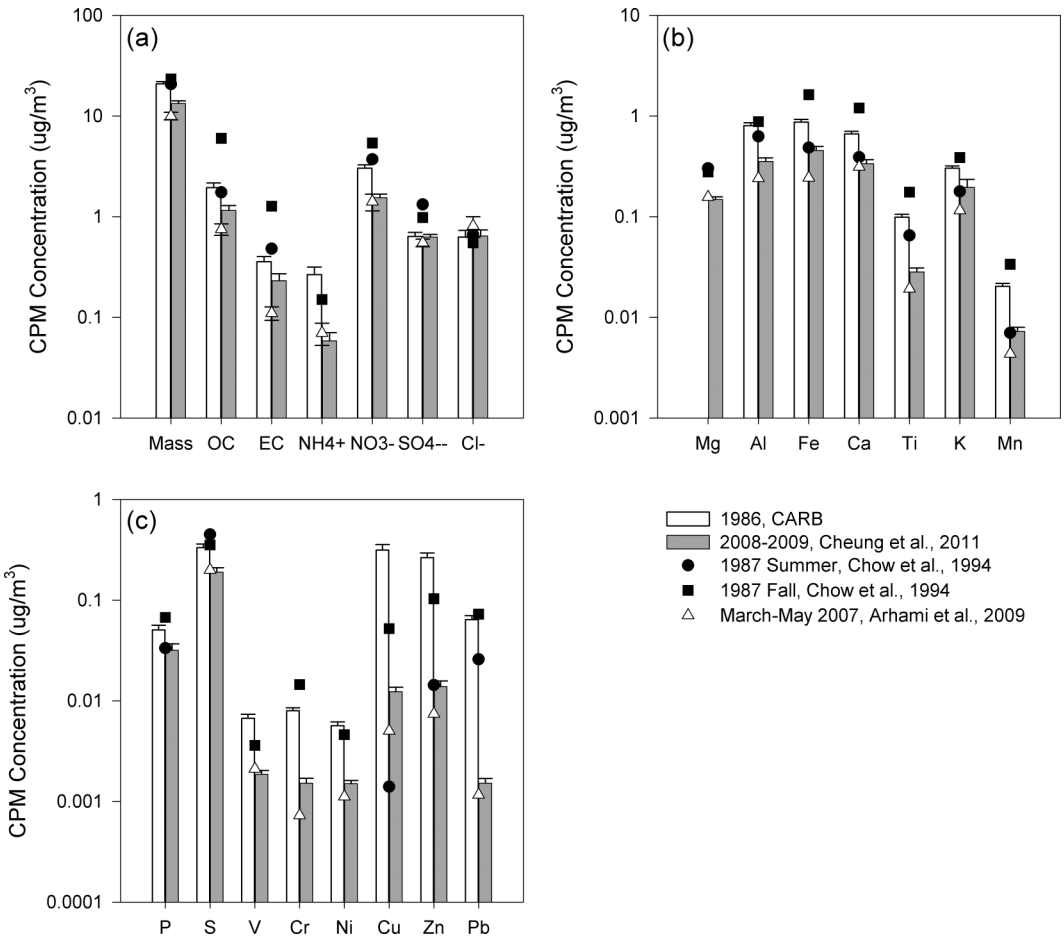

Figure 6. CPM concentrations of (a) mass, organic and elemental carbon, and inorganic ions; (b) elements of crustal origins; and (c) elements of anthropogenic origins in Long Beach. Error bars show standard errors of the average when available.

Combustion emissions from vehicles, industries, and ships

Although particles from combustion sources mostly reside in the fine mode, the "upper tail" of that source function can extend to the lower range of the CPM fraction. For example, Huang and Yu (2008) demonstrated that elemental carbon (EC), a tracer of vehicular emissions, experienced a bimodal pattern in both ambient and tunnel environments, with a major fine mode and a minor coarse mode. Studies conducted in the Los Angeles Basin in the 20th century also demonstrated that, although dominant in the fine PM fraction, metals emitted by combustion sources could also contribute to a minor fraction of CPM (Krudysz et al., 2008; Singh et al., 2002).

The tailpipe emissions of CPM is often associated with high emitting and poorly controlled vehicles (Kleeman et al., 1999). In downtown Los Angeles, CPM elemental carbon was reduced from an annual average level of 0.55 $\mu g/m^3$ to 0.42 $\mu g/m^3$ from 1986 to 1995 (23% reduction), and further to 0.08 $\mu g/m^3$ (80% reduction) from 1995 to 2008 (Figure 5a). The sampling sites in Riverside were located in residential areas adjacent to major roadways, and again, a similar reduction trend was observed (29% reduction from 1986 to 1995 and 71% reduction from 1995 to 2008) (Figure 7a). The U.S. EPA requires automobiles of 1975 model year and after to be equipped with catalytic converters to control tailpipe emissions. In 1984, the Smog Check Program was implemented in California. In addition to various emission standards adopted for light-duty vehicles, heavy-duty diesel trucks, and bus engines in the 1990s, a number of programs were developed to remove the older and more polluting cars from the road. For example, California's Carl Moyer Program has provided funding to encourage the retrofit and replacement of diesel engines in an effort to reduce emissions from diesel-powered vehicles and equipment. In the last decade, the SCAQMD also adopted/amended a few rules to promote cleaner on-road vehicles used by the public sector. The high reductions of EC, particularly after the 1990s, highlight the effectiveness of various controls implemented by the regulatory agencies to control tailpipe emissions.

In addition to tailpipe emissions, industrial activities also serve as potential sources of CPM in this basin. Metal processing facilities could emit high levels of heavy metals, including Fe, Cu, Zn, As, Cd, and Pb (Newhook et al., 2003). In particular, smelters could release metals in the coarse size range either as stack or fugitive emissions (Chan et al., 1983; Harrison and Williams, 1983), and could contribute to the high levels of Cu, Zn, and Pb in 1986 as shown in Figures 5–7. In 1992, the SCAQMD adopted Rule 1420 to reduce emissions of lead—one of the six criteria pollutants identified by the U.S. EPA. This regulation requires all emission points of a lead-processing

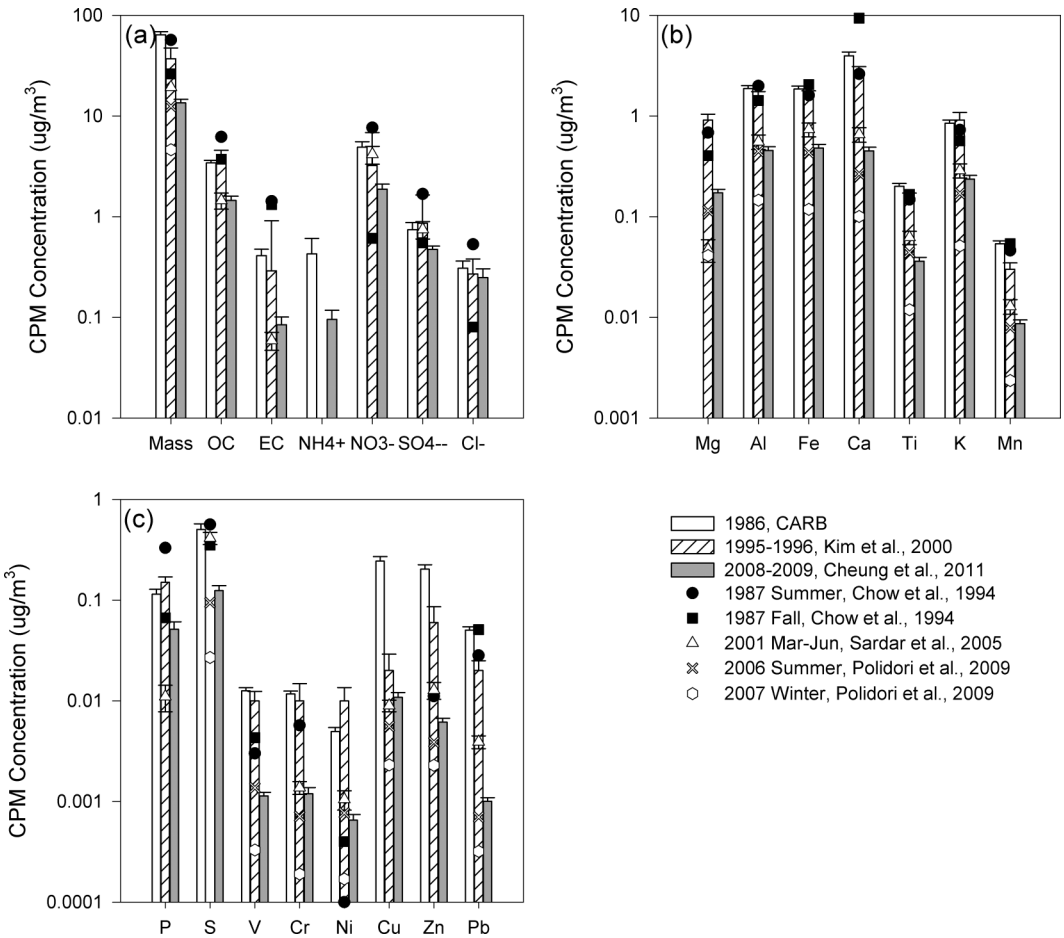

Figure 7. CPM concentrations of (a) mass, organic and elemental carbon, and inorganic ions; (b) elements of crustal origins; and (c) elements of anthropogenic origins in Riverside. Error bars show standard errors of the average when available.

facility (including facilities that produce lead oxide, brass, and bronze) to be vented to an emission collection system. Furthermore, facilities are required to conduct air quality monitoring at their property lines, in addition to the source-oriented monitors placed by the SCAQMD at or beyond the facilities' fence lines. The high reductions of Cu, Zn, and Pb from 1986 to 1995 (96%, 84%, and 69%, respectively, in downtown Los Angeles) could largely result from the effective control of emissions from metal processing facilities.

Oil refinery is also a major source of industrial emissions. Various coarse elements, including Pb, Ce, La, Zn, V, Cu, Co, and to a lesser extent Cr, Ni, and Mo, could be emitted from refinery fluid catalytic cracking stacks (Campa et al., 2011). Using principal component analyses, Pakbin et al. (2011) showed that CPM-bound Ni and Cr are markers of industrial emissions, with V originating from ship emissions in the Los Angeles/Long Beach Harbor based on coarse particles sampled from 2008 to 2009. In general, the lower concentrations of these elements in the coarse mode support that they originate from combustion sources in this basin. In downtown Los Angeles, the reductions of V, Cr, and Ni were higher from 1995 to 2008 (>90% reduction calculated using 1995 and 2008 data), compared with those from 1986 to 1995 (Figure 5c). In Riverside, the corresponding reductions of Ni, Cr, and V were 93%, 88%, and 89%, respectively, from 1995 to 2008, consistent with the observations in downtown Los Angeles. The significant reductions after 1995 could be resulting from series of regulations targeted to control emissions from stationary sources, as evident by the reductions in PM_{10} emissions from industrial processes and manufacturing and industrial sources from 1995 to 2010 according to the emission inventory of the South Coast Air Basin acquired from CARB. For example, Rule 1105.1, aiming to reduce PM_{10} and ammonia emissions from fluid catalytic cracking units used in petroleum refineries, was adopted in 2003. Additionally, the Los Angeles/Long Beach ports approved an incentive program that promotes the use of cleaner-burning fuel in cargo ships transiting within 40 miles of the Bay and at berth in 2008. Note that the efforts to control ship emissions began in the early 20th century, consistent with the historical trend of vanadium, which experienced similar annual averages in 1986 and 1995, with higher reduction rates from 1995 to 2008. Therefore, the high reductions of Ni, V, and Cr after 1995 could be due to various programs and incentives that aim to reduce combustion-related emissions from vehicles and industries, as well as the efforts to reduce ship emissions from harbor activity.

CPM-bound lead (Pb) also decreased considerably in the Los Angeles Basin. Pb could originate from brake wear and wheel

weights, gasoline exhaust, and oil combustion as the extended upper tail of the fine PM mode, as well as metal processing industries (Harrison and Williams, 1983; Isakson et al., 2001; Pakbin et al., 2011). In downtown Los Angeles, Pb levels have decreased from an annual mean of 0.097 $\mu g/m^3$ to 0.030 $\mu g/m^3$ from 1986 to 1995, and further to 0.0023 $\mu g/m^3$ in 2008. As discussed previously, the early reduction of Pb could be resulted from Rule 1420, which was adopted in 1992 aiming to control lead emissions. The latter reduction (after 1995) could partly be attributed to the complete elimination of the sales of leaded fuel for use in on-road vehicles in 1996. In Long Beach, ships (Isakson et al., 2001) and refineries emissions (Newhook et al., 2003) could also be potential sources of lead. The reduction in CPM lead concentrations in Long Beach was comparable to those observed in downtown Los Angeles (0.064 $\mu g/m^3$ in 1986 to 0.0015 $\mu g/m^3$ in 2007). Recent studies (Pakbin et al., 2011; Root, 2000), including a study of CPM in Los Angeles and Long Beach conducted in 2008, indicated that Pb is now predominantly sourced from vehicular abrasion. Therefore, it is likely that the Pb reductions in the last two decades were largely driven by the phase-out of Pb in gasoline vehicles, as well as controlled emissions from various industries as discussed previously.

Vehicle abrasion

Particles originating from vehicular abrasion contribute to road dust PM, though the mass-fraction is typically small. Cu, which is present in brake linings as lubricants, is often used as tracers of brake wear in areas where industrial emission of Cu is not significant (Lin et al., 2005; Pakbin et al., 2011). Note that the high concentrations of Cu in 1986 likely resulted from emissions of metal processing industries, as discussed in the previous section, and therefore Cu might not be a reliable tracer of brake wear back in the 1980s. Nonetheless, a recent study in the Los Angeles Basin suggested that majority of coarse particulate Cu was generated from the wear of brake linings based on CPM sampled from 2008 to 2009. Despite the considerable decrease of elements from combustion origins from 1995 to 2008 (Pakbin et al., 2011), the reduction of Cu was less significant in the same period. In Los Angeles, the higher annual average concentrations of Cu in 2008 compared with the 1995 levels could be due to the increased emissions from tire and brake wear from the greater number of both light-duty and heavy-duty vehicles on the road. The contribution of anthropogenic sources to elements, including Cu, is generally higher in Los Angeles and Long Beach than Riverside (Cheung et al., 2011a). From 1995 to 2008, the lower reduction of Cu (46%) relative to other CPM species with anthropogenic origins (89%, 88%, and 93% for V, Cr, and Ni, respectively) in Riverside further confirms the lower reduction of non-tailpipe mobile source emissions. The reduction of Cu might also be a "side benefit" as a result of the high reduction of mineral dust in Riverside.

Inorganic ions

In general, reductions of CPM inorganic ions were relatively lower than combustion related CPM due to their natural origins and, to a lesser extent, secondary formation. Nitrate is the most abundant inorganic species in the coarse fraction, accounting for an average of 17% of CPM mass in this basin (Cheung et al., 2011a). In the Los Angeles Basin, nitrate is primarily formed by sea salt depletion, a process involving the reaction of nitric acid with sodium chloride (Zhuang et al., 1999), and to a lesser extent the reactions with mineral dust and the condensation of alkaline salts on CPM surfaces when sea salt levels are low (Cheung et al., 2011b). In downtown Los Angeles and Riverside, the level of nitrate was reduced by 13% and 34%, respectively, from 1986 to 1995, whereas corresponding reductions were 38% and 42% from 1995 to 2008. Substantial efforts have been made to reduce emissions of nitrogen oxides, as demonstrated by the reduction of nitrogen oxides (NO_x) emissions from 1561 tons per day (TPD) in 1985 to 1332 TPD in 1995 and 742.2 TPD in 2010 in the South Coast Air Basin (Emission Inventory of CARB). In addition to the regulations to control mobile emissions as described previously, the SCAQMD has adopted a few rules to control NO_x emissions from stationary sources, including boilers and process heaters from refineries, cement kilns, gas melting furnaces, and stationary gas turbines. Since 2001, the Los Angeles ports incorporated a voluntary vessel speed reduction program with the objective of reducing both NO_x and PM emissions by decreasing the vessel's speed to 12 knots near the ports. The control of NO_x emissions may have an indirect effect on the reduction of coarse particulate nitrate by limiting the levels of its precursors, which could also decrease the CPM-bound nitrate associated with the hygroscopic growth of nitrate originally in the fine PM mode (Geller et al., 2004; Seinfeld and Pandis, 2006). In addition, the reduction of mineral dust, which could serve as a reaction site for nitrate (Usher et al., 2003), might have also indirectly reduced the levels of nitrate in CPM. Sulfate, on the other hand, has several potential sources, namely water-soluble gypsum and sea salt sulfate, as well as the upper tail of ammonium sulfate, and the reduction was insignificant. Chloride, primarily originating from sea salt in the coarse mode, is used as a tracer of fresh sea salt aerosols. Cl^- levels increased from 0.37$\mu g/m^3$ in 1995 to 0.55 $\mu g/m^3$ in 2008 in downtown Los Angeles. This could be due to yearly variations in sea salt level, as well as the reduction in nitrogen oxides emissions, which decreased the rate of sea salt depletion and increased the levels of unreacted chloride.

Crustal enrichment factors

The use of crustal enrichment factors (CEFs) allows for an examination of the contributions of anthropogenic versus crustal sourced elements associated with CPM in current and earlier measurements in this basin (Lawson and Winchester, 1979). In general, elements with CEFs close to 1 are indicative of crustal origins, whereas higher CEFs (>10) are considered to originate from sources other than crustal materials. To calculate CEF, the CPM concentration of each element was normalized to Al and then divided by its relative abundance to Al in the upper continental crust (UCC) acquired from Taylor and McLennan (1985). Polidori et al. (2009) studied the size-fractionated indoor and outdoor CEFs at four retirement homes located in San Gabriel Valley (east of downtown Los Angeles and west of Riverside) and Riverside in 2006 to 2007. In general, CEFs were higher in San Gabriel Valley than Riverside. S, Cu, Zn, Mo, and Pb were the elements with CEFs >10 in the coarse mode

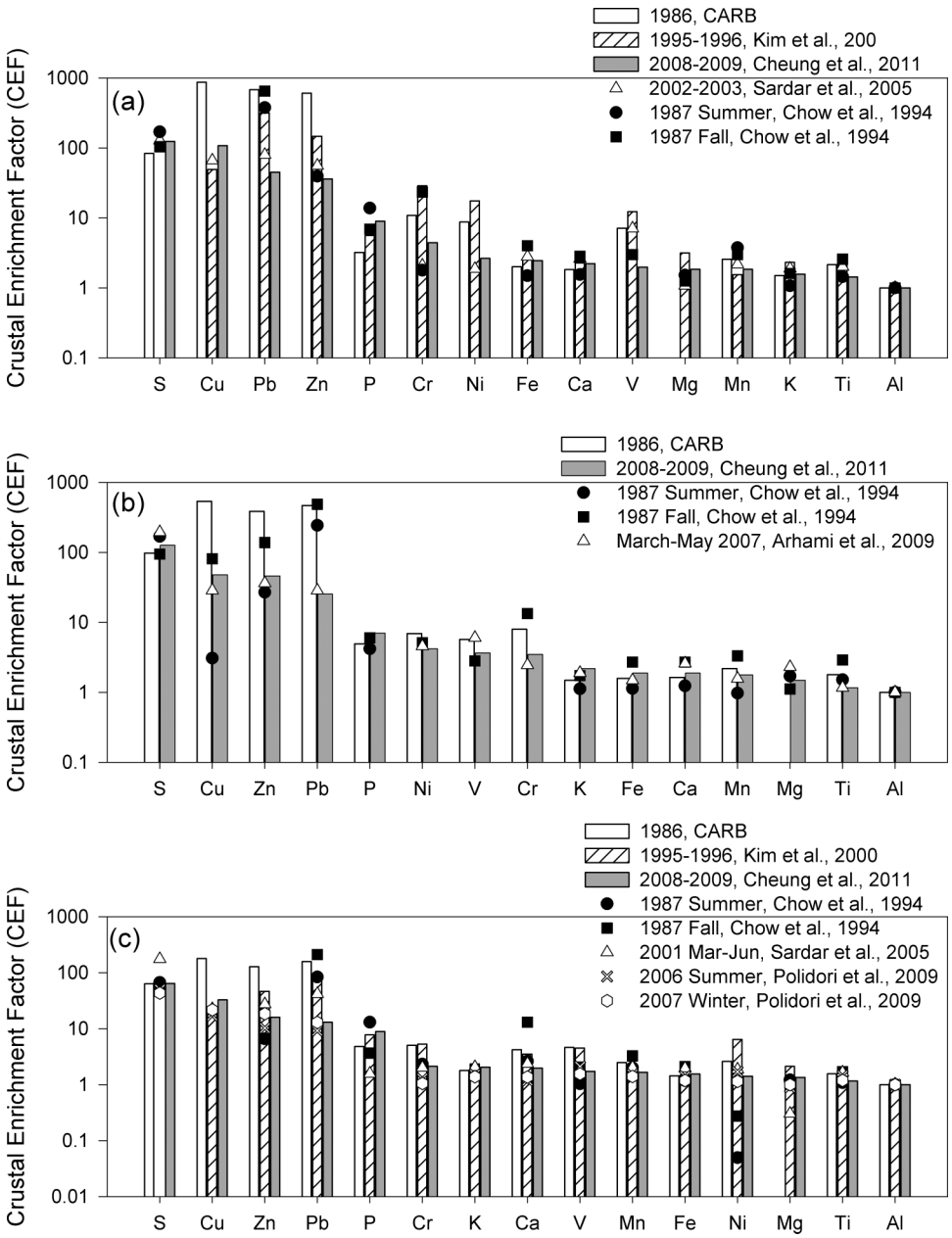

Figure 8. Crustal enrichment factors in (a) downtown Los Angeles, (b) Long Beach, and (c) Riverside.

in all four retirement homes, whereas the CEFs of Na, Ba, Cr, and Ni were high only in the three San Gabriel sites. In the comprehensive CPM study conducted at 10 samplings sites in Los Angeles from 2008 to 2009 (Cheung et al., 2011a), the investigators found higher CEFs in Los Angeles and Long Beach than Riverside for most of the elements examined, highlighting the higher contribution of anthropogenic sources to CPM in urban Los Angeles. Sb and Sn, commonly used as lubricants in brake pads (Chan and Stachowiak, 2004), were the most highly enriched elements (CEFs >100) in all the 10 sampling sites, highlighting the impact of brake wear in the coarse mode.

Figure 8a–c shows the CEFs for selected elements measured at each study in downtown Los Angeles, Long Beach, and Riverside, respectively. Across the three regions, the highest CEFs were found for S, Cu, Zn, and Pb. Sulfur has various sources in the coarse mode, including mineral dust, sea salt, secondary formation, and lubricants in brake pads. The comparable CEFs of sulfur in both spatial and temporal terms suggest that past air quality regulations were not effective in controlling all sources, or that the reduction of one source has been counterbalanced by the increased contribution from other sources. Most of the regulations targeted particulate emissions of combustion origins and were therefore more likely to reduce the levels of fine particles as opposed to those in the coarse fraction. Natural PM sources are not the targets of controls, as evident by the comparable levels of chloride particles—a tracer of sea salt—in the last few decades. Therefore, the reduction of sulfur originating from

sea salt might be insignificant. The CEFs of Pb were reduced by more than an order of magnitude from 1986 to 2008, due to the regulations to control the level of Pb in gasoline as well as emissions from ships and industries. In downtown Los Angeles, Pb, Zn, Cu, Cr, Ni, and V all exhibited CEFs >10 in the 1986 and 1995 data sets. In 2008, Cu, Pb, and Zn were the only elements that had CEFs of 10 or higher, suggesting that ship and industrial emissions, the dominant sources of Cr, Ni, and V, were no longer a significant contributor to CPM in downtown Los Angeles in recent years. Although fewer studies were conducted in Long Beach, the limited data show a consistent pattern to that observed in downtown Los Angeles. Sulfur, along with elements generated from vehicular abrasion such as Cu, are the major anthropogenic components of CPM particles in 2008. CEFs of anthropogenic elements were much higher in the relatively stagnant conditions in Long Beach in 1987 (CEF = 81, 138, and 486 for Cu, Zn, and Pb, respectively) (Chow et al., 1994), likely due to the enhancement of particle resuspension by heavy-duty vehicle–induced turbulences when wind speed and mixing height was low. The lower CEFs of Ni and V in 1987 in Long Beach were unexpected given the proximity of this sampling site to the ports, where oil combustion and refinery emissions are major sources of PM in this area (Krudysz et al., 2008). In general, CEFs were lower in Riverside than downtown Los Angeles and Long Beach, consistent with its suburban nature. S, Cu, Zn, and Pb were the most enriched (CEFs >10) elements in Riverside. The more recent 2008 data set shows that the CEFs of Zn and Pb have gone down after 1995, whereas the CEFs of Cu and S remained comparable from 1995 to 2008. Note that road dust is a mixture of natural dust and anthropogenic materials. Therefore, the reduction of enrichment factor could be due to the increased contribution of road dust compared with other anthropogenic sources that contained lower levels of Al. In general, the CEFs were higher in cooler periods than warmer periods, as demonstrated in both the studies by Chow et al. (1994) and Polidori et al. (2009), in which seasonal variations were examined. This further confirms that traffic-induced turbulence becomes a source of resuspended material in winter when the mixing height is lower, consistent with the results from a study that observed higher contribution from vehicular emissions in cooler periods in this basin (Pakbin et al., 2011).

Summary and Conclusions

Overall, PM_{10} mass concentration has decreased by approximately half from 1988 to 2009 since the PM_{10} standard was put in place in 1987. PM_{10} daily concentrations from downtown Los Angeles and Long Beach show compliance with the federal EPA PM_{10} standard, while violating the more stringent California standard. These two sites also demonstrated equivalency for the current PM_{10} and proposed $PM_{10-2.5}$ standards. On the other hand, both PM_{10} and CPM levels were higher in Riverside as highlighted by some violations of the federal standards in late 1980s and early 1990s. This site also demonstrates that the proposed CPM standard is more stringent than the current PM_{10} standard. The reduction trends of combustion-related CPM namely EC, V, Cr, and Ni were higher after 1995, consistent with the implementation of $PM_{2.5}$ standard in 1997. The CEF of Cu, a tracer of brake wear, has remained comparable or increased after 1995, suggesting that the contribution of brake wear to CPM has become more significant despite the overall reduction in CPM mass since 1995. In general, the reduction of CPM mass was mostly driven by the reduction of mineral dust, whereas reduction of contributions from inorganic ions and non-tailpipe vehicular emission were less significant from 1995 to 2008.

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