

Report to the California Legislature

**AMBIENT AIR CONCENTRATIONS
OF MANGANESE IN CALIFORNIA**

A Report Submitted By:

California Air Resources Board

As required by Health and Safety Code § 41511.5

July 2011



Edmond G. Brown Jr., Governor

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ACRONYMS AND ABBREVIATIONS

ARB	California Air Resources Board
dichot	dichotomous
EPA	Environmental Protection Agency
Mn	manganese
MATES	Multiple Air Toxics Exposure Study
MMAD	mass median aerodynamic diameter
n.d.	no data
ng/m ³	nanograms per cubic meter
OEHHA	Office of Environmental Health Hazard Assessment
PM	particulate matter
PM10	particulate matter 10 microns or less in MMAD
PM2.5	particulate matter 2.5 microns or less in MMAD
REL	reference exposure level
SCAQMD	South Coast Air Quality Management District
TAC	toxic air contaminant
TSP	total suspended particulates

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1. Introduction

State law (Health and Safety Code Section 41511.5) requires the Air Resources Board (ARB) to conduct a study of ambient air concentrations of manganese (Mn) to determine if there are areas of the state that have unhealthy concentrations of this toxic air contaminant (TAC). This law requires ARB to submit a report to the Legislature describing the conclusions of the study and provide any necessary recommendations for reducing ambient air exposures.

ARB evaluated the statewide ambient air monitoring data and found that manganese levels are below the level of health concern established by California's Office of Environmental Health Hazard Assessment (OEHHA). This report provides a summary of the ARB staff evaluations and results. The potential health effects of concern from manganese are symptoms of neurotoxicity that were identified in occupational settings with much higher exposures than are seen in the ambient air in California.

2. Air Quality Monitoring for Manganese

Air monitoring for manganese is routinely conducted as part of California's network for measuring toxic air contaminants. Manganese has also been measured in special monitoring studies. ARB staff's evaluation of manganese included review of the following data:

- Annual-average manganese 2007-2009
- Retrospective analysis of manganese 1990-2000
- South Coast Air Quality Management District's MATES III 2004-2006

ARB maintains a toxics monitoring network of 17 monitoring stations statewide, measuring ambient concentrations of up to 64 substances (Figure 1). The monitoring data are typically sampled, analyzed, and reported as 24-hour-average concentrations. These 24-hour averages provide the basis for calculating annual-average concentrations.

The annual-average concentrations are compared to health effects benchmarks developed by OEHHA. For manganese, OEHHA set a long-term chronic reference exposure level (REL) of 90 nanograms per cubic meter (ng/m^3) in total suspended particulates (TSP). The chronic REL is the level at which adverse health effects would not be expected from continuous lifetime exposure of the general public, including sensitive populations. OEHHA also developed a short-term 8-hour reference exposure level of $170 \text{ ng}/\text{m}^3$.



Figure 1 – Toxic air contaminant (TAC) monitoring sites in California

3. 2007-2009 Monitoring

The monitoring results show that annual-average concentrations of manganese at all sites were substantially below OEHHA’s chronic reference exposure level of 90 ng/m³ in TSP. Table 1 (Appendix II) provides the annual-average concentrations of manganese measured in TSP at each of the 17 monitoring sites for the years 2007, 2008, and 2009, and the 3-year average of each site. The 3-year average ranged from 8 to 38 ng/m³, all well below the chronic REL for long-term exposure. Figure 2 shows the combined annual averages at each site for the three-year period of 2007-2009 compared to the OEHHA reference level.

The daily 24-hour monitoring data was also evaluated at each site for comparison to OEHHA’s short-term reference exposure level. The shortest averaging time available in the monitoring network is 24 hours, which was compared to the OEHHA short-term REL for an 8-hour average. The 8-hour REL is a concentration at or below which adverse non-cancer health effects would not be anticipated for repeated 8-hour exposures. None of the manganese concentrations exceeded this short-term REL.

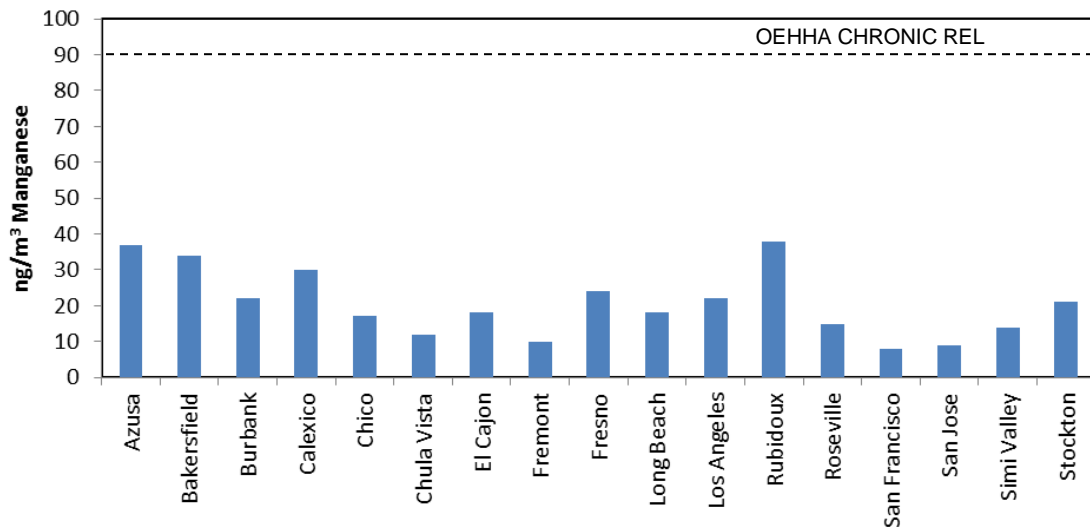


Figure 2 – Annual-average manganese concentrations in TSP (2007-2009)

The combined annual averages are shown for 2007-2009 compared to the chronic REL of 90 ng/m³ established by OEHHA. This report relies solely on the OEHHA reference exposure levels since U.S. EPA’s reference concentration is currently under review.

4. Retrospective Analysis 1990-2000

Manganese and other trace metals were routinely measured during the 1990’s from samples of total suspended particulates (TSP). Figure 3 shows a retrospective analysis from 1990 to 2000. During that period, the statewide annual-average concentrations ranged from 20 to 30 ng/m³, well below OEHHA’s chronic REL of 90 ng/m³.

In addition to using measurements from TSP, manganese concentrations were measured as part of ARB’s routine dichotomous (dichot) monitoring program from 1990 through 2001 at 15 sites throughout California. The dichot sampler measured manganese in both the PM_{2.5} (0 to 2.5 μm) and coarse (2.5 to 10 μm) particle size fractions. An analysis showed that manganese is primarily associated with the coarse fraction of particulate matter rather than PM_{2.5} fraction (Table 2 in Appendix II). In 14 of the 15 sites, the concentration of manganese in the coarse PM fraction was 3 to 11 times higher than that in the PM_{2.5} fraction. The sum of the PM_{2.5} and coarse fractions provides a measure of total manganese from inhalable particles in the size range of PM₁₀ or smaller. All of the annual-average concentrations were below the OEHHA chronic REL of 90 ng/m³.

Both the current ARB monitoring results and the retrospective analysis demonstrate that statewide ambient air manganese concentrations have remained remarkably consistent over the past two decades. In addition, manganese exposure for the average Californian remains at levels well below what is considered hazardous by OEHHA.

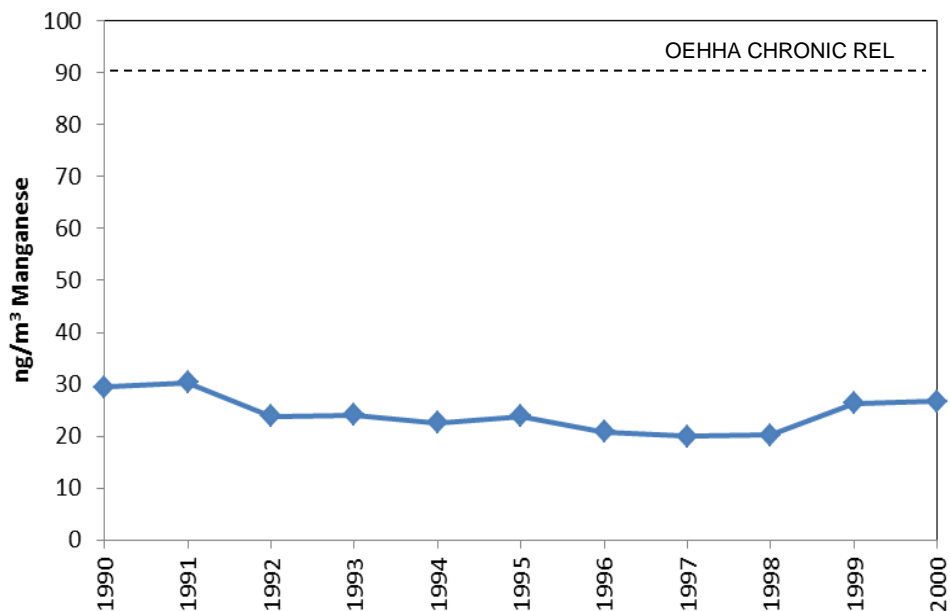


Figure 3 – Statewide annual-average manganese concentrations in TSP (1990-2000)

5. SCAQMD Special Study (MATES III 2004-2006)

MATES III was a monitoring and evaluation study conducted in the South Coast Air Basin by the South Coast Air Quality Management District from 2004 to 2006. The final report was released in September 2008 [1]. MATES III consisted of several elements including a monitoring program, an emission inventory of toxic air contaminants, and carcinogenic risk modeling for the basin. As part of this study, manganese was measured at ten sites in the South Coast Air Basin.

TSP monitoring was conducted for a two-year period from April 2004 to March 2006 at ten sites. Typically, samples were collected over a 24-hour period and all individual results for a site within a year were averaged to produce an annual average. The combined annual averages for the two-year periods are presented in Figure 4 and Table 3 (Appendix II). These results show that none of the sites had a two-year average that exceeded OEHHA’s chronic REL. Further analysis of the individual 24-hour-average data points found only two samples that exceeded OEHHA’s 8-hour REL of 170 ng/m³. No samples from ARB’s ongoing statewide toxic air contaminant monitoring program have exceeded OEHHA’s 8-hour REL for manganese since the MATES III time period.

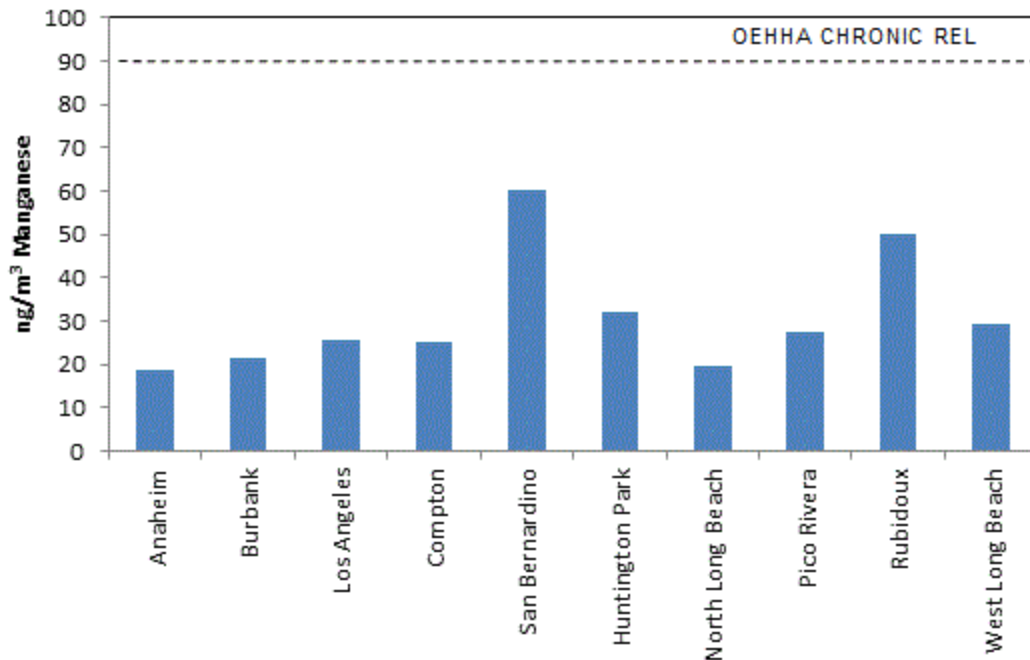


Figure 4 – Annual-average manganese concentrations in TSP from SCAQMD’s MATES III (2004-2006)

Two-year average of manganese measurements (2004-2006). Annual averages were calculated by averaging all values from a site. Note: Huntington Park and North Long Beach only had data for Year 1 (2004-2005) of the study.

6. Summary

Manganese is identified as a toxic air contaminant under state law, and the California Office of Environmental Health Hazard Assessment (OEHHA) has established a chronic reference exposure level (REL) of 90 ng/m³ for ambient air exposure to manganese from TSP. The chronic REL is a long-term exposure level at which adverse health effects are not likely to occur. The California Air Resources Board routinely monitors manganese and other toxic air contaminants at 17 sites around the state. In addition, special monitoring studies have been conducted in which manganese is measured along with other trace metals.

Recent results from ARB’s ongoing toxic air contaminant program show annual-average manganese concentrations substantially below OEHHA’s reference exposure level for manganese. Similar results were found in the review of long-term monitoring data as far back as 1990, as well as in two additional short-term monitoring studies. Considering that no monitoring site exceeds OEHHA’S chronic REL on an annual basis, and the large safety factors built into the calculation of the OEHHA guideline, no areas were determined to have unhealthy ambient air concentrations of manganese.

7. Reference

SCAQMD (2008) Multiple Air Toxics Exposure Study III (MATES III) Final Report
<http://www.aqmd.gov/prdas/matesIII/MATESIIIFinalReportSept2008.html>
(accessed 3/7/2011)

Appendix I – Assembly Bill 294 Text

The text to AB294 is as follows:

The people of the State of California do enact as follows:

SECTION 1. Section 41511.5 is added to the Health and Safety Code, to read:

41511.5. The state board shall conduct a study of ambient air concentrations of manganese in the state to determine if there are areas in the state that have unhealthy concentrations of manganese. No later than January 1, 2010, the state board shall submit a report to the Legislature that describes the conclusions of this study and provides recommendations for reducing manganese exposures as needed.

Appendix II – Tables of Annual-average Manganese Concentrations

Table 1 – Annual-average manganese concentrations in TSP (2007-2009)				
Location	2007 (ng/m³)	2008 (ng/m³)	2009 (ng/m³)	3-Year averages^a (ng/m³)
Azusa	36	45	28	37
Bakersfield	30	48	23	34
Burbank	21	25	21	22
Calexico	40	27	25	30
Chico	14	24	12	17
Chula Vista	13	12	11	12
El Cajon	24	19	14	18
Fremont	11	10	8	10
Fresno	25	30	16	24
Long Beach	19	18	16	18
Los Angeles	20 ^b	27	21	22
Rubidoux	43	43	29	38
Roseville	13	20	13	15
San Francisco	9	9	6	8
San Jose	11	11	7	9
Simi Valley	15	16	11	14
Stockton	24	26	13	21

^aCombined annual average of the monthly averages for years 2007, 2008, and 2009.

^b*Italics* indicates one or more months are missing data.

Table 2 – Annual-average manganese concentrations from the ARB dichotomous monitoring program for 1991, 1995, and 1999^a

Location	PM2.5 Mn concentrations (ng/m ³)			Coarse Mn concentrations (ng/m ³)			Coarse Mn to PM2.5 Mn ratios		
	1991	1995	1999	1991	1995	1999	1991	1995	1999
Azusa	17.2	19.6	21.9	25.5	18.6	16.7	1.5	0.9	0.8
Bakersfield	n.d.	n.d.	2.6	n.d.	n.d.	20	n.d.	n.d.	7.7
Calexico	n.d.	7.9	6.6	n.d.	23.1	23	n.d.	2.9	3.5
Corcoran	n.d.	2.8	2.1	n.d.	20.7	22	n.d.	7.4	10.7
Coso Junction	n.d.	n.d.	1.5	n.d.	n.d.	7.6	n.d.	n.d.	5.1
Fresno	3.2	2.7	2.6	16.5	14.7	16.0	5.2	5.4	6.2
Modesto	3.2	2.3	2.6	14.2	9.0	14.9	4.4	3.9	5.7
North Long Beach	n.d.	4.2	3.2	n.d.	8.1	9.5	n.d.	1.9	3.0
Portola	n.d.	n.d.	1.6	n.d.	n.d.	15.3	n.d.	n.d.	9.6
Sacramento	n.d.	2.0	2.1	n.d.	12.9	11.0	n.d.	6.5	5.2
San Jose	2.7	1.9	1.9	7.7	5.4	6.2	2.9	2.8	3.3
Stockton	4.5	4.4	4.8	14.5	11.2	13.8	3.2	2.5	2.9
Tuft College	n.d.	1.5	1.6	n.d.	10.9	13.6	n.d.	7.3	8.3
Victorville	n.d.	n.d.	3.4	n.d.	n.d.	14.7	n.d.	n.d.	4.3
Visalia	4.5	2.0	3.1	24.9	12.8	19.5	5.5	6.4	6.3

n.d. – no data

Calculations of manganese annual-average concentrations were based upon the combination of quarterly averages.

^aThe concentration of manganese in the TSP fraction of particulate matter can be estimated from the concentration of manganese in the PM10 fraction (the sum of the concentrations of the PM2.5 and coarse manganese fractions) using a conversion factor of 0.55 (see Appendix III). Using this factor, the manganese concentration values for all sites listed in Table 2 would be below the OEHHA chronic REL of 90 ng/m³ with a range of 13 to 78 ng/m³.

Table 3 – Annual-average manganese concentrations in TSP from SCAQMD’s MATES III (2004-2006)			
Location	Year 1 (4/04 to 3/05) averages (ng/m³)	Year 2 (4/05 to 3/06) averages (ng/m³)	Combined average^a (ng/m³)
Anaheim	19	18	19
Burbank	21	23	22
Los Angeles	25	26	26
Compton	25	25	25
San Bernardino	62	59	60
Huntington Park	32	n.d.	32
North Long Beach	19	20	20
Pico Rivera	27	n.d.	27
Rubidoux	48	52	50
West Long Beach	29	30	29

n.d. – no data

^aCombined 2-year average of samples from Year 1 and Year 2. The concentration of manganese was determined from TSP samples. Note: Only Year 1 data are available for the Huntington Park and Pico Rivera sites.

Appendix III – Converting Manganese Concentrations in PM10 to TSP

The health guidelines published by OEHHA are based on manganese from TSP samples. Therefore, to make full use of manganese monitoring data from other fractions of PM, staff performed a regression analysis using TSP and PM10 data from the Fresno site of ARB's monitoring network. Staff found that approximately 55% of the mass of TSP is in the PM10 fraction. These results are similar to previously published data by U.S. EPA¹ and ARB.² This figure shows the results of the analysis.

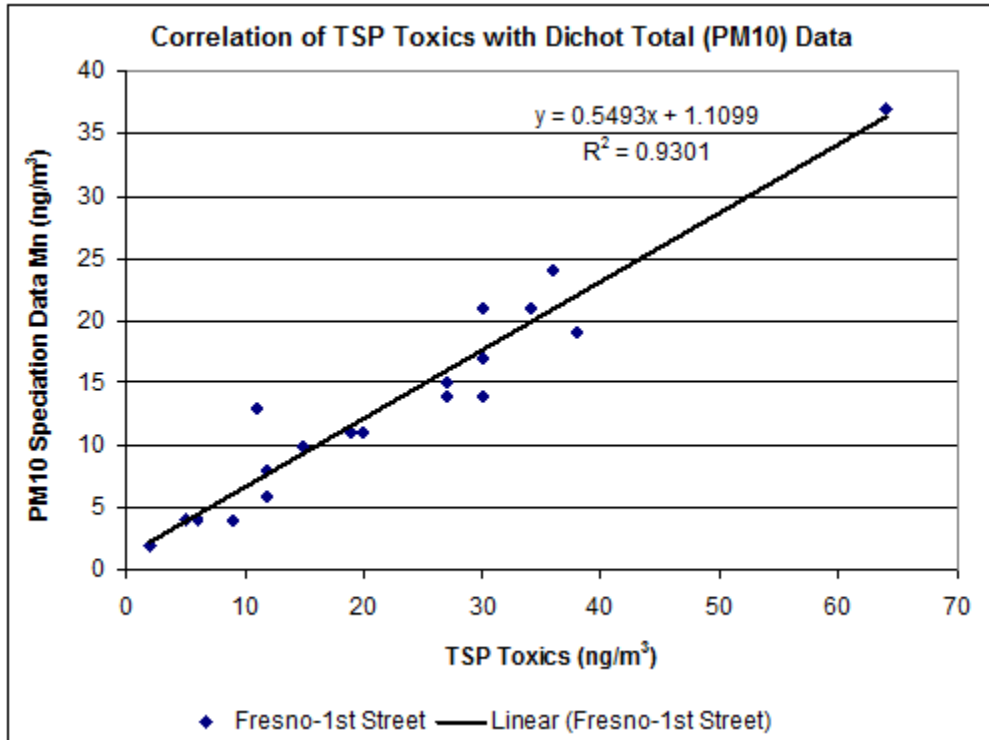


Figure 5 – Manganese concentrations in PM10 and TSP samples

¹ U.S. EPA 2004: Air Quality Criteria for Particulate Matter (Final Report, Oct 2004). <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=87903#Download>

² Houck JE: 1989 "Determination of Particle Size Distribution Composition of Particulate Matter from Selected Sources in California", ARB Contract A6-175-32. http://www.arb.ca.gov/research/single-project.php?row_id=46346.