

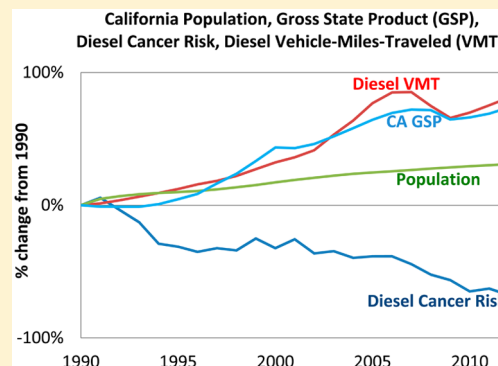
# Ambient and Emission Trends of Toxic Air Contaminants in California

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## S Supporting Information

**ABSTRACT:** After initiating a toxic air contaminant (TAC) identification and control program in 1984, the California Air Resources Board adopted regulations to reduce TAC emissions from cars, trucks, stationary sources, and consumer products. This study quantifies ambient concentration and emission trends for the period 1990–2012 for seven TACs that are responsible for most of the known cancer risk associated with airborne exposure in California. Of these seven, diesel particulate matter (DPM) is the most important; however DPM is not measured directly. Based on a novel surrogate method, DPM concentrations declined 68%, even though the state's population increased 31%, diesel vehicle-miles-traveled increased 81%, and the gross state product (GSP) increased 74%. Based on monitoring data, concentrations of benzene, 1,3-butadiene, perchloroethylene, and hexavalent chromium declined 88–94%. Also, the ambient and emissions trends for each of these four TACs were similar. Furthermore, these declines generally occurred earlier in California than elsewhere. However, formaldehyde and acetaldehyde, which are formed in the air photochemically from volatile organic compounds (VOCs), declined only 20–21%. The collective cancer risk from exposure to these seven reviewed TACs declined 76%. Significant reduction in cancer risk to California residents from implementation of air toxics controls (especially for DPM) is expected to continue.



## INTRODUCTION

**Background.** In response to public concern about exposure to airborne carcinogens, California adopted the Toxic Air Contaminant (TAC) Identification and Control Act in 1984.<sup>1</sup> Since then, California has identified 21 TACs for which California's Office of Environmental Health Hazard Assessment (OEHHA) has developed inhalation cancer potency factors,<sup>2</sup> and the Air Resources Board (ARB) has implemented regulations such as airborne toxic control measures (ATCMs) to limit TAC emissions. In 1987, California adopted the Air Toxics "Hot Spots" Information and Assessment Act, which requires operators of significant-risk facilities to reduce risks from exposure to emitted TACs.<sup>3</sup> The 1990 U.S. Clean Air Act Amendments<sup>4</sup> listed 187 "hazardous air pollutants" that California added to its TAC list in 1993, although no ATCMs have been adopted for added TACs. Since then, the U.S. EPA has developed National Emission Standards for Hazardous Air Pollutants (NESHAPs)<sup>5</sup> that are delegated to the states. Local California agencies may adopt more stringent regulations than statewide ATCMs or federal NESHAPs.

Several studies have reviewed ambient TAC trends. Mobile sources of TACs have been studied in California, especially benzene.<sup>6–13</sup> These studies show declining ambient concentrations with implementation of emissions control regulations. In particular, California gasoline reformulation in 1996 led to a large decline in benzene emissions and ambient concentrations.<sup>7–11</sup> Because ambient diesel PM (DPM) concentrations are not measured directly, two surrogates have been

used to estimate their trends: coefficient of haze (COH)<sup>14</sup> and elemental carbon (EC).<sup>15,16</sup> Some studies show declines in ambient TAC concentrations nationally<sup>17–19</sup> and in specific states.<sup>20–23</sup> For some TACs, although limited literature was found on statewide or air-basin-wide ambient concentration trends, reductions in ambient TAC concentration have been observed at specific locations due to targeted emission controls.<sup>24–26</sup>

The study objectives were to (1) quantify ambient and emission trends for TACs in California and estimate the associated trend in cancer risk, (2) review relationships between declines in ambient concentrations and emissions controls in California, and (3) compare ambient trends in California with trends elsewhere based on data from previous studies.

**TACs Studied/Selected.** Table 1 shows the seven TACs selected for review, along with their principal sources, years identified, and unit risk factors. Cumulatively, they account for most of the known chemically induced cancer risk from exposure to Californians during the 1990–2012 study period, with particulate matter from diesel-fueled engines (DPM) the most important in terms of overall cancer risk.

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Table 1. Toxic Air Contaminants Reviewed<sup>a</sup>

toxic air contaminant	principal source	year identified	unit risk factor ( $\mu\text{g}/\text{m}^3$ ) <sup>-1</sup>
diesel particulate matter (DPM)	mobile sources	1998	$8.94 \times 10^{-4}$
benzene	mobile sources	1985	$8.12 \times 10^{-5}$
1,3-butadiene	mobile sources	1992	$4.87 \times 10^{-4}$
hexavalent chromium	chrome plating	1986	$4.54 \times 10^{-1}$
perchloroethylene	dry cleaning	1991	$1.71 \times 10^{-5}$
formaldehyde	atmospheric reactions	1992	$1.71 \times 10^{-5}$
acetaldehyde	atmospheric reactions	1993	$8.12 \times 10^{-6}$

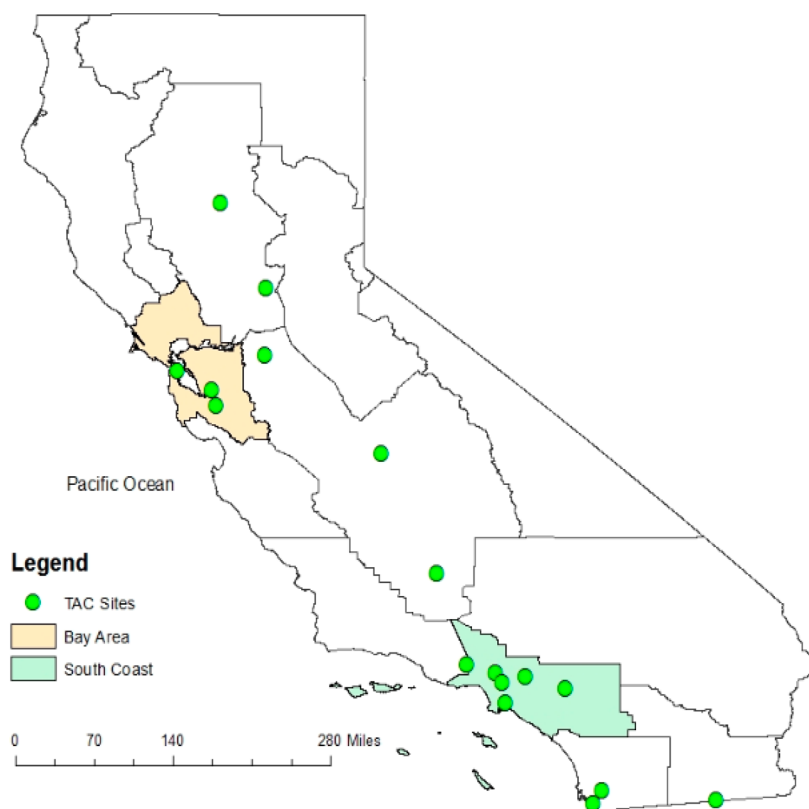
<sup>a</sup>California's Toxic Air Contaminant Identification Reports for each TAC are available at [www.arb.ca.gov/toxics/id/summary/summary.htm](http://www.arb.ca.gov/toxics/id/summary/summary.htm), which provides links to "health risks" and "exposure assessment" documents.

Three of these TACs have been emitted mainly from mobile sources: DPM, benzene, and 1,3-butadiene. Although some stationary sources use diesel-fueled engines, most DPM is emitted from mobile sources—mainly trucks, buses, and off-road sources such as ships.<sup>27</sup> Benzene is emitted mainly from on-road vehicles—from incomplete fuel combustion and from gasoline evaporation.<sup>27</sup> Its tropospheric lifetime is about 10 days, allowing dispersion throughout an air basin.<sup>28</sup> 1,3-Butadiene is emitted mainly from incomplete fuel combustion from mobile sources.<sup>30</sup> Its tropospheric lifetime is typically a few hours.<sup>31</sup>

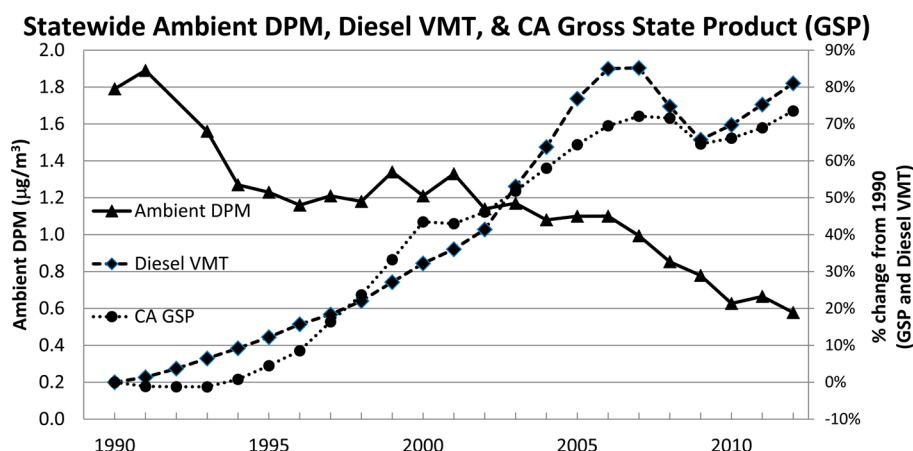
Two of these TACs have been emitted mainly from stationary sources: perchloroethylene and hexavalent chromium. Perchloroethylene has been used as a solvent, especially for dry cleaning, and in various product formulations.<sup>32</sup> Its atmospheric lifetime is about four months, sufficiently long that global background levels have been reported.<sup>33</sup> Chromium compounds have two oxidation states: trivalent and hexavalent; in the 1980s, 3–8% of total chromium in California ambient air was hexavalent.<sup>34</sup> Hexavalent chromium has been used for chrome plating. Its half-life was estimated to be about 13 h (~19 h lifetime).<sup>35</sup> For both of these TACs, most exposure occurs on a neighborhood scale, with health risks highest near point sources.<sup>27</sup>

The remaining two TACs result mainly from photochemical reactions of emitted VOCs: formaldehyde and acetaldehyde. U.S. field studies have shown that primary emissions account for only 8–30% of ambient formaldehyde concentrations, depending on location.<sup>36–38</sup> Photolysis is the main removal mechanism for formaldehyde, leading to a lifetime of about 4 h. Reaction with hydroxyl radical is the main removal mechanism for acetaldehyde, leading to a lifetime of about 9 h.<sup>28</sup> Rain and fog also remove airborne aldehydes.

Four other TACs were considered for inclusion,<sup>27</sup> but not reviewed. For carbon tetrachloride, persistent worldwide concentrations represent significant cancer risk; however, emissions have been minimal for decades. For *p*-dichlorobenzene, California's recent ambient data are usually below the limit of detection (LOD). For methylene chloride, California's ambient data exhibits such variability that data quality was



**Figure 1.** ARB's toxic air contaminant (TAC) long-term monitoring network. Seventeen sites (circles) provided data for most of 1990–2012. The two most populous air basins are shaded: South Coast and San Francisco Bay Area. Seven sites (not shown) that operated for shorter periods also provided data: Richmond and Upland (ended 1997); Fontana (ended 1999); Concord, Modesto, and Santa Barbara (ended 2000); and San Pablo (1997–2000).



**Figure 2.** Statewide diesel PM ambient concentrations, diesel VMT (million vehicle miles traveled by diesel vehicles), and California Gross State Product (GSP). DPM concentrations are based on  $\text{NO}_x$  concentrations and DPM/ $\text{NO}_x$  emissions ratios. Note: VMT decline 2007–2009 was due to a national economic downturn (the “Great Recession”).

questionable. For dioxins, the lack of long-term ambient monitoring data precluded a level of review comparable to the seven TACs reviewed.

## MATERIALS AND METHODS

**Data Sources.** Emission inventories were obtained from the California Emissions Projection Analysis Model (CEPAM)<sup>39</sup> and the California Emission Inventory Development and Reporting System (CEIDARS).<sup>40</sup> CEPAM/Norcal Version 1.04 was used to provide a consistent methodology from which DPM emissions for 1990–2012 were calculated. ARB’s emission factor model EMFAC2011<sup>41</sup> was used to provide input into CEPAM/Norcal Version 1.04 for on-road mobile source emissions. CEIDARS (run-date: October 15, 2014) was used for the other TACs; it provides TAC inventories in two-year increments, for 1996–2012. CEIDARS incorporates CEPAM data and data from local air districts for stationary sources. Speciation profiles were used to estimate TAC emissions from particulate matter and VOCs. These emission inventories take into account the effects of growth and emission controls. The data presented here may differ from some previously reported values; emission inventory values change due to improved emission profiles and activity data.

Ambient DPM concentrations were estimated using oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) as a surrogate, combined with scaling factors derived from the ratio of DPM emissions to total  $\text{NO}_x$  emissions as obtained from the ARB inventory. Basin-wide annual average ambient  $\text{NO}_x$  concentrations (1990–2012) were calculated using hourly average measurements from over 200 monitoring sites. The following assumptions were made: (1) ambient DPM concentrations are proportional to  $\text{NO}_x$  concentrations in each air basin; (2) emissions are well-mixed on basin-wide time scales, and (3) background  $\text{NO}_x$  concentrations can be neglected. Section S-IV, Methodology for Estimating Ambient DPM Concentrations, provides details (S = Supporting Information).

The ARB started a TAC monitoring network in 1985 (Figure 1). At sites selected to represent basin-wide and statewide averages, ambient air samples have been collected and speciated for TACs.<sup>42</sup> TAC trends were derived using all monitoring sites in the ARB’s air quality database.<sup>43</sup> Considering the earliest years for which reliable ambient data (late 1980s) and emission

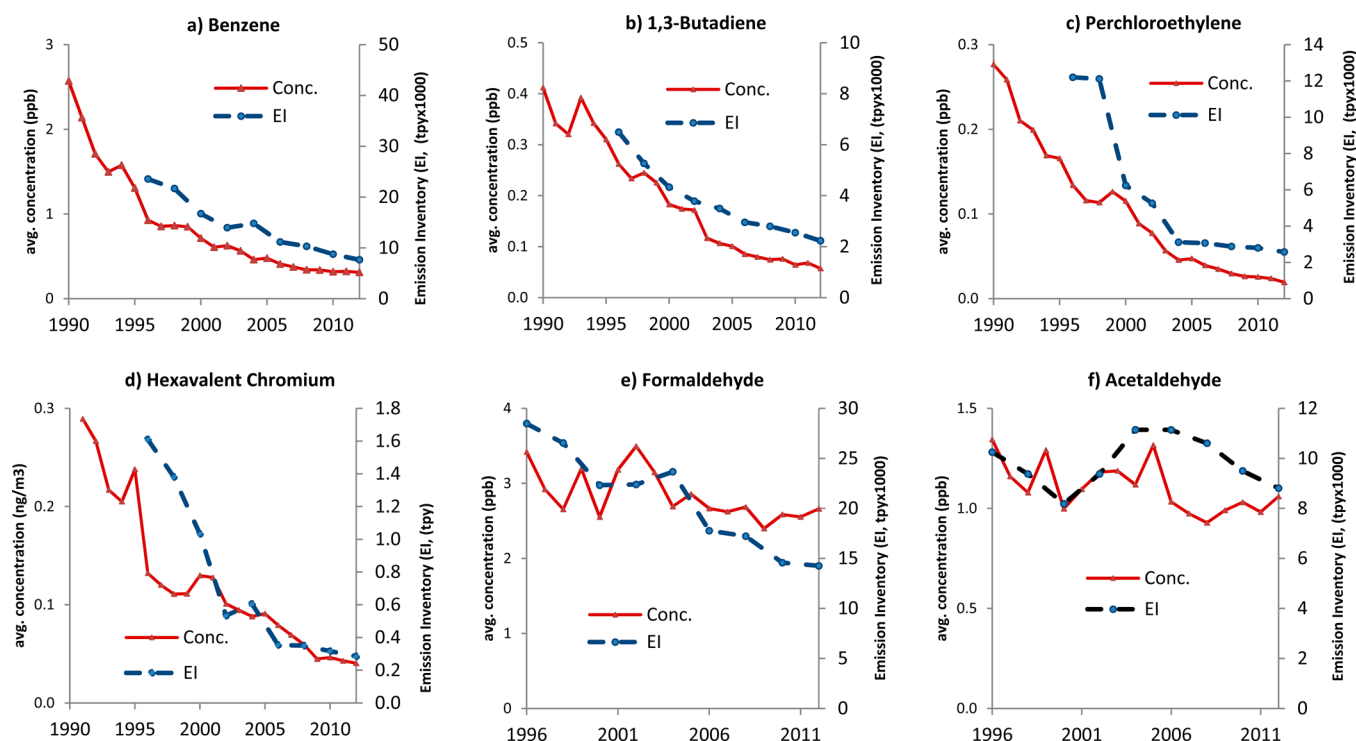
inventory data (1990) were available, 1990 was used as the starting point for this study.

The Bay Area Air Quality Management District (BAAQMD) also started a TAC monitoring network that same year in the San Francisco Bay Area Air Basin (SFBAAB, Figure S1).<sup>44</sup> Some sites were chosen based on regional concerns, such as proximity to oil refineries;<sup>44</sup> others were collocated with ARB sites. Based on correlations between BAAQMD and ARB data sets for perchloroethylene and benzene (Figure S2), data from all ARB and BAAQMD sites that operated for most of the 1990–2012 period were combined to obtain a more robust data set for trend analyses of these TACs in the Bay Area. Because only limited BAAQMD data were available for other TACs, no other data sets were combined.

The South Coast Air Quality Management District has conducted four Multiple Air Toxics Exposure Studies (MATES) in the South Coast Air Basin (SoCAB). This paper uses data from MATES-II (1998–1999),<sup>45</sup> MATES-III (2004–2006),<sup>46</sup> and MATES-IV (2012–2013).<sup>47</sup> Data from MATES-I (1987) were not readily comparable due to differences in objectives and sites. Data from national air monitoring networks—National Air Toxics Trends Stations (NATTS), Urban Air Toxics Monitoring Program (UATMP), Photochemical Assessment Monitoring Stations (PAMS)—were not used, due to limited data in California (NATTS, UATMP), or systematic problems in benzene measurement (PAMS).<sup>13</sup> However, comparisons were made with U.S. EPA data that include NATTS and/or UATMP monitoring sites.<sup>48</sup>

**Determination of Cancer Risk.** Ambient DPM concentrations were inferred from the scaling factors described above. For TACs other than DPM, annual mean ambient concentrations were determined by aggregating data from all sites, weighed equally. Half of the LOD and 75% completeness criteria were used for this determination, which is consistent with U.S. EPA methodology.<sup>49</sup> Annual means were calculated as the average of monthly means.

The statewide cancer risk resulting from exposure to each TAC was defined as the number of new cases of cancer projected to occur per million residents. That risk was calculated for each TAC by multiplying its statewide yearly average ambient concentration by its unit risk factor (Table 1). These TAC unit risk factors were derived from OEHHA’s inhalation cancer potency factors, inhalation exposure rates,



**Figure 3.** Statewide annual average concentrations and emissions inventory (EI) trends for six toxic air contaminants. EI data were available starting in 1996. (a) Benzene (1990–2012), (b) 1,3-Butadiene (1990–2012), (c) Perchloroethylene (1990–2012), (d) Hexavalent Chromium (1991–2012), (e) Formaldehyde (1996–2012), (f) Acetaldehyde (1996–2012).

individual sensitivity factors, and exposure factors, using the methodology outlined in OEHA's 2012 risk assessment guidelines.<sup>50</sup> These guidelines require the selection of breathing rates; this study used the 95th percentile daily breathing rate (DBR) for children under 2 years old and the 80th percentile DBR for all other ages.<sup>51</sup>

## RESULTS AND DISCUSSION

Results are presented by source type: mobile source TACs, stationary source TACs, and secondary TACs. Figure 2 shows the statewide ambient DPM trend, and Figure 3 shows annual statewide ambient and emissions trends for the six other TACs reviewed. Figure S3 shows these latter trends normalized, with trend lines added for SFBAAB and SoCAB. Table S1 shows the associated data with standard errors, as well as summarized MATES data. MATES data and ARB's SoCAB data show similar ambient declines.

**Mobile Source TACs. Diesel Particulate Matter (DPM).** Figure 2 shows that between 1990 and 2012, statewide ambient DPM concentrations declined 68% (3.1%/year), while vehicle-miles-traveled (VMT) for diesel-fueled vehicles increased 81%,<sup>52</sup> and California's Gross State Product (GSP) increased 74% (in constant dollars).<sup>53</sup> This period coincides with ARB's adoption of several diesel-related emission control regulations (Table S2). The 32% decline for 1990–2000 is close to the projected 40% emission reduction from ARB's regulatory program.<sup>54</sup> In 2000, ARB's Diesel Risk Reduction Plan<sup>55</sup> (DRRP) recommended the replacement and retrofit of diesel-fueled engines (e.g., diesel particulate filters), and the use of ultra-low-sulfur (<15 ppm) diesel fuel. Implementation of the DRRP resulted in a 49% decline for 2000–2010, and the ARB expects a decline of 71% for 2000–2020.<sup>56</sup> This expectation of a steeper decline is due to state truck regulations that have

accelerated fleet turnover, with BC emissions reductions of  $\geq 40\%$  between 2009 and 2011 in Los Angeles.<sup>57</sup>

**Benzene.** Figure 3a shows that ambient benzene concentrations declined 88% from 1990 to 2012. This decrease was achieved despite increased population (31%) and VMT (30%) during that period (Figure S4). Figure 3a shows similar ambient and emissions trends, indicating an association between regulatory measures and reduced ambient concentrations. Tailpipe emissions data from ARB's vehicle surveillance program show that the 2003 fleet-average benzene rate decreased by 89% relative to the 1995 fleet.<sup>58</sup> Table S3 lists major regulations that reduced mobile source emissions and their expected emission reductions, if available.

Two ARB programs significantly reduced mobile source emissions, including benzene: cleaner fuels and vehicle emission controls. The ARB's Low-Emission Vehicles (LEV) regulations<sup>59</sup> resulted in reduced emissions of nonmethane organic gases (NMOG) from new light- and medium-duty vehicles. LEV I regulations (1994) led to reduced exhaust and evaporative emissions of hydrocarbons. Since 1996, light-duty vehicles sold in California have been equipped with California's second generation On-Board Diagnostic (OBD-II) system. About half of total car emissions resulted from malfunctions related to emission control devices,<sup>60</sup> thus OBD-II implementation led to reduced benzene emissions by facilitating repairs.

ARB's Phase II Reformulated Gasoline (RFG-2) regulation required a reduction in benzene volume content from 1.7% to  $\sim 1\%$ ,<sup>30,61</sup> which was confirmed at several service stations.<sup>6,11</sup> Between 1995 and 1996, vehicular benzene emissions declined 54%; most of this reduction was attributed to lowered levels of benzene and related aromatics in gasoline.<sup>7</sup> The benzene percentage of NMOG (nonmethane organic compounds) in tunnel emissions declined from 6% in 1995 to 3.6–4.2% in later



years.<sup>6</sup> RFG-2 implementation was projected to cause a 24% decline in ambient concentration,<sup>30</sup> but greater reductions occurred. From 1995 to 1996, the decline was 29%, which was attributed to implementation of RFG-2.<sup>61</sup> In a SFBAAB tunnel, the benzene/VOC weight fraction declined 39% between 1995 and 1996,<sup>11</sup> while SFBAAB ambient concentrations also declined 39% between 1995 and 1996 (Table S1). In the SoCAB, RFG-2 was implemented over two years (1994–1996), and benzene concentrations declined 40% (Table S1) over that period.

Based on these results, a link has been established between RFG-2 implementation and benzene concentration decline. However, other regulations have allowed multiyear implementation, making it difficult to link emission controls and TAC concentration declines. Furthermore, mobile sources tend to have overlapping vehicle and fuel regulatory implementations.

**1,3-Butadiene.** Figure 3b shows that annual average 1,3-butadiene concentrations declined 85% from 1990 to 2012, and also that ambient and emissions trends are similar. Table S3 lists major regulations that reduced 1,3-butadiene emissions. 1,3-Butadiene emissions depend upon fuel composition, engine type, emission control devices, operating temperature, and the age and condition of the engine,<sup>62</sup> and were expected to decline due to implementation of motor vehicle regulations.<sup>29</sup> Tailpipe emissions data from ARB's vehicle surveillance program show that the 2003 fleet-average 1,3-butadiene rate decreased by 86% relative to the 1995 fleet.<sup>58</sup> The adoption of technology-forcing emissions standards led to three-way catalysts to control vehicle exhaust. Vehicles equipped with effective exhaust catalysts emitted less than a tenth as much 1,3-butadiene as those without functioning catalysts.<sup>63,64</sup> LEV I regulations (1994) led to reduced exhaust and evaporative emissions of hydrocarbons.

**Stationary Source TACs. Perchloroethylene.** Figure 3c shows that statewide ambient perchloroethylene concentrations declined 92% (1990–2012), and also shows similar ambient and emissions trends. Table S4 lists regulations that reduced perchloroethylene emissions, and their expected emissions reductions. In 1980, the BAAQMD adopted a rule controlling perchloroethylene emissions from dry cleaners, which led to a 1981 ARB Suggested Control Measure.<sup>65</sup> By 1993, eight local air districts had rules that required a carbon absorber or refrigerated condenser, and dry-cleaners were transitioning from vented transfer machines to vented dry-to-dry machines and closed-loop machines.<sup>65</sup>

In 1993, California adopted a regulation to limit emissions of perchloroethylene from dry cleaning that projected a 78% reduction in emissions from dry cleaners and an overall emissions reduction of 47% (1994–1998; Table S4).<sup>65</sup> Figure 3c shows a lower (33%) ambient decline during that period, perhaps due to lesser emission reductions from other sources, such as degreasing and paint. Due to local air district rules, perchloroethylene concentrations declined steeply before the mid-1990s, when the ARB's 1993 dry cleaner regulation was implemented.

Starting in 2003, California provided financial incentives for dry cleaners to use other solvents.<sup>32</sup> From 2003 to 2005, perchloroethylene emissions from dry cleaning decreased by ~70%.<sup>32</sup> Subsequently, the ARB adopted a regulation for automotive products that prohibited the use of perchloroethylene,<sup>66</sup> and regulations banning perchloroethylene use in aerosol coatings and most consumer products.<sup>67</sup> ARB's dry cleaning regulation was amended in 2007 to require phase-out

of perchloroethylene machines by 2023, which would reduce emissions to minimal levels.<sup>32</sup>

**Hexavalent Chromium.** Figure 3d shows that ambient concentrations of hexavalent chromium declined 86% (1991–2012). Before 1991, the ARB's monitoring method allowed conversion of hexavalent to trivalent chromium;<sup>35,68</sup> therefore, reliable monitoring data are only available since 1991. The ambient decline appears steeper prior to 1996; this may reflect a decrease in chrome plating operations, or a switch from hexavalent to trivalent chromium for plating.<sup>27</sup> Figure 3d also shows some correspondence between the ambient and emissions trend.

Table S4 lists ARB-adopted regulations to control hexavalent chromium emissions and their expected emissions reductions. ARB's 1988 chrome plating regulation required ≥95% emission reductions, and was expected to reduce emissions by 97% within four years.<sup>69</sup> In 1993, the U.S. EPA adopted a NESHAP<sup>70</sup> with the same emission reduction goal; the ARB regulation was modified in 1998 for conformity.<sup>71</sup> In 2005, hexavalent chromium emissions from these facilities were 99.97% less than in 1987, which was more than expected from implementation of these regulations. A 2006 ARB regulation further reduced these emissions, by requiring add-on air pollution control devices and chemical fume suppressants.

Table S4 shows three additional regulations that led to reduced emissions. A 1989 ARB regulation prohibited the use of hexavalent chromium in cooling towers.<sup>72</sup> Others prohibited the use of hexavalent chromium in motor vehicle and mobile equipment coatings (2001), and in thermal spraying operations (2005).

Significant emissions reductions resulted from the 1980s regulations, prior to the ARB's 1991 adoption of a reliable hexavalent chromium analytic method for its ambient monitoring network. Therefore, prior to ARB regulations, hexavalent chromium concentrations in the 1980s were probably much higher than the 1991 statewide average.

**Secondary TACs (Formaldehyde and Acetaldehyde).** For the period 1996–2012, Figures 3e and 3f show that ambient concentrations of formaldehyde declined 22%, and acetaldehyde declined 21%. (Before 1996, the monitoring method underestimated actual concentrations, but no correction factor is available.<sup>27</sup>) During the same period, these figures also show that formaldehyde emissions declined 50%, and acetaldehyde emissions declined 14%. The ambient and emission trends for each aldehyde do not correspond as well as for other TACs, which is likely related to the dominance of their photochemical formation versus direct emissions.

The ARB promulgated a series of increasingly stringent emission standards for motor vehicle exhaust to limit hydrocarbon emissions, which also limited aldehyde emissions. For example, the ARB's 1990 Low Emission Vehicle/Clean Fuels (LEV/CF) regulations were expected to reduce formaldehyde emissions from cars and light-duty trucks over several years.<sup>73</sup> Comparing tailpipe average emission rates between the 1995 and 2003 fleets, formaldehyde emissions declined 11%/year and acetaldehyde emissions declined 8.6%/year.<sup>58</sup> Based on emissions monitoring in a SFBAAB tunnel (1994–1999), formaldehyde emissions decreased by 10%/year, and acetaldehyde by 9.5%/year; attributed to implementation of RFG-2 in 1996.<sup>74</sup> A subsequent SFBAAB tunnel study found that the formaldehyde emission factor declined 12%/year between 2001 and 2006, and the acetaldehyde emission factor declined 3.8%/year. These declines were attributed to vehicle fleet turnover

Table 2. Ambient Toxic Air Contaminant Trends: Comparison with Data from Other Sources

period	this study		other sources		
	location	decline (%/yr)	location	decline (%/yr)	reference
Diesel PM					
1990–2000	CA (California)	3.2%	CA	5.5% (COH)	Kirchstetter <sup>14</sup>
1990–2012	CA	3.4%	CA	3.0% (BC)	Bahadur <sup>15</sup>
2005–2012	CA South Coast	7.9%	CA South Coast	9.1%	MATES-IV <sup>47</sup>
Benzene					
1989–1993	CA	10%	Canada	5.0%	Dann 1995 <sup>83</sup>
1994–2000	CA	9.2%	National	7.8%	Cook 2004 <sup>22</sup>
1994–2002	CA	7.5%	National	9.3%	Fortin 2005 <sup>13</sup>
1994–2009	CA	5.2%	National	4.4%	EPA 2010 <sup>81</sup>
2003–2010	CA	6.2%	National	4.7%	EPA 2014 <sup>19</sup>
1990–2008	CA	4.8%	Camden NJ	3.7%	NJ DEP 2011 <sup>20</sup>
1995–1996	SF Bay Area (CA)	40%	SF Bay Area (CA)	39% (tunnel) 42% (ambient)	Kirchstetter 1999 <sup>11</sup> Harley 2006 <sup>6</sup>
1998–2005	Burbank, CA	11% (Ln)	London, UK	26% (Ln)	Warneke 2012 <sup>10</sup>
1,3-Butadiene					
1994–2008	CA	5.6%	Camden NJ	5.1%	NJ DEP 2011 <sup>20</sup>
1995–2003	CA	6.5%	Canada	5.0%	Curren 2006 <sup>85</sup>
2003–2010	CA	6.4%	CA	6.4%	EPA 2014 <sup>82</sup>
Perchloroethylene					
1991–2006	CA	5.7%	eight states	2.6%	EPA 2010 <sup>81</sup>
2003–2010	CA	7.8%	CA	5.9%	EPA 2014 <sup>82</sup>
			National	7.7%	
Hexavalent Chromium					
2005–2010	CA	7.8%	National	4.9%	EPA 2014 <sup>82</sup>
Formaldehyde					
2003–2010	CA	2.6%	National	2.4%	EPA 2014 <sup>82</sup>
Acetaldehyde					
2003–2010	CA	2.1%	National	2.7%	EPA 2014 <sup>82</sup>

and fuel reformulation that occurred during that period; the higher formaldehyde decline was attributed to the contemporaneous switch from MTBE (a formaldehyde precursor) to ethanol in gasoline.<sup>75</sup>

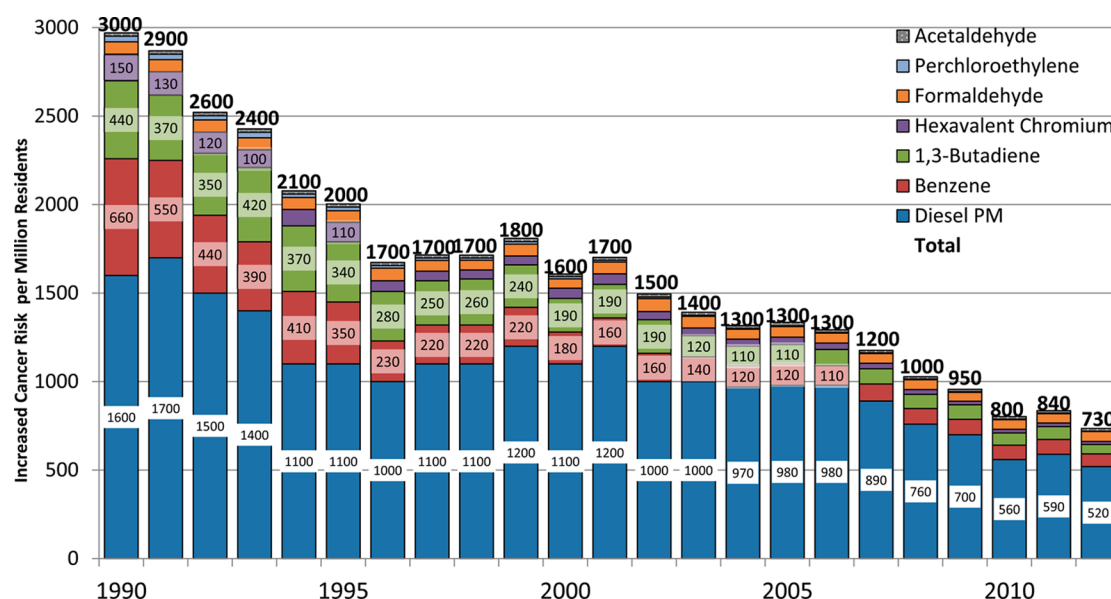
Because incomplete oxidation of ethanol yields acetaldehyde, increased use of ethanol in transportation fuels could lead to an increase in ambient acetaldehyde concentrations. However, other components of California gasoline, such as aromatic compounds and alkenes, were found to be primarily responsible for the formation of acetaldehyde.<sup>76</sup> Figure 3f shows no increase in acetaldehyde concentrations between 2002 and 2004, when MTBE in gasoline was replaced with ethanol in California.<sup>75</sup>

Although aldehydes are present in the ambient air mainly due to photochemical processes, they are also directly emitted. The major aldehyde direct emission source is combustion, especially from on-road motor vehicles. The largest area-wide source is residential wood burning. Because formaldehyde is used in composite wood products and consumer products, formaldehyde also has significant nonmobile emission sources. An ARB regulation adopted in 2008 was designed to reduce formaldehyde emissions from composite wood products by 57%, or 500 tons per year.<sup>77</sup> Although this represents only 2.4% of primary emissions, these sources cause disproportionately high exposure due to indoor off-gassing.

**Comparison with Ambient Trends Obtained from Other Studies.** Table 2 compares ambient TAC declines (%/year) from this study with available reported values, such as from U.S. EPA's NATTS monitoring network.<sup>78</sup> These trend comparisons are expressed as relative changes over time. This table

shows linear reduction rates for the starting and ending years of data for the same period as for each reference provided, except for Burbank and London where natural logarithms (Ln) are compared.<sup>10</sup>

**Mobile Sources.** Because diesel PM is not measured directly, it is difficult to compare ambient DPM trends. However, DPM estimates from MATES-III<sup>46</sup> and -IV<sup>47</sup> show a 64% decrease in ambient concentration (2005–2012) for SoCAB, compared to a 55% decrease in SoCAB based on this paper's methodology. (Table S5 shows ambient DPM concentrations for individual air basins.) Table 2 compares the DPM trend from this study with MATES and estimates that result from use of other surrogates, and Figure S5 graphs the comparison with COH<sup>14</sup> and EC (equivalent to BC)<sup>15</sup> trends. BC was calculated from COH data,<sup>14</sup> but COH monitoring was phased out around 2000. The IMPROVE monitoring network<sup>79</sup> was used to obtain EC measurements,<sup>15</sup> although this network is mainly in rural areas. Using 1990–2000 data from 11 SFBAAB sites, COH declined about 55%;<sup>14</sup> compared to a contemporaneous 32% decline in statewide DPM (Figure 2). Possible causes for this disparity are (1) reduced agricultural burning during this period<sup>80</sup> (most COH sites were in or near agricultural burning areas), and (2) reduced EC/DPM ratios (COH concentrations are proportional to EC concentrations),<sup>14</sup> as observed between MATES-II and -III periods.<sup>46</sup> A review of 1990–2012 data from IMPROVE sites found that wildfires led to spikes in EC levels in some years. Overall, these data showed a statewide 60% EC decline, similar to the trend in fossil fuel EC emissions (primarily DPM);<sup>15</sup> compared to the 68% decline in statewide DPM in this study. These comparative



**Figure 4.** Cumulative increased cancer risk for seven toxic air contaminants, per million California residents. Values are rounded to two significant figures. Hexavalent chromium values prior to 1991 and aldehyde values prior to 1996 were obtained by linear extrapolation from the three subsequent years. Due to unavailability of 1992 DPM emission inventory, 1992 DPM cancer risk is the average of 1991 and 1992 values. Nonlabeled bars represent cancer risk <100 per million residents.

trends provide some validation of the scientific reliability of this study's methodology.

Benzene ambient trends from this study were compared with trend data from 22 sites in ten other states for 1994–2009,<sup>81</sup> and from 154 national trend sites for 2003–2010.<sup>19,82</sup> The trend lines appear parallel (Figure S6), but the national trend lags California's trend by several years. For 1994–2009, national concentrations declined 66% compared to 78% in California; for 2003–2010, the declines were 33% (national) and 43% (California). In Camden NJ, benzene declined 66% (1990–2008)<sup>20</sup> compared to 87% in California. In Canada, benzene declined 20% (1989–1993)<sup>83</sup> compared to 50% in California. These data all show steeper declines in benzene concentrations in California, presumably because California initiated regulations earlier than elsewhere. However, in London, benzene declined 91% (1998–2008),<sup>10</sup> compared to 61% for that period in California. This was attributed to London's post-1998 adoption of mobile source controls that California had adopted earlier.<sup>10</sup> In New York, the benzene decline (~50%, 1990–2003) was found to be consistent with California's decline; major reasons included the adoption of RFG regulations and California's LEV program.<sup>84</sup>

For 1,3-butadiene, recent national data (2003–2010)<sup>19,82</sup> show the same decline in ambient concentrations as found in California from this study. However, data for earlier periods show a steeper decline in California compared to other locations, as follows. Concentrations declined 66% in Camden NJ (1994–2008),<sup>20</sup> compared to California's 78%. Concentrations at Canadian urban sites declined 38% (1995–2003),<sup>85</sup> compared to California's 61%; consistent with earlier regulations in California.

The 89% ambient benzene decline and the 88% ambient 1,3-butadiene decline (both 1990–2012) could be compared with the 65% reduction in ROG emissions reported in the SoCAB (1993–2012).<sup>86</sup> This indicates that regulations targeting mobile-source TACs have been effective.

**Stationary Sources.** For the period 1991–2006, the U.S. EPA provided ambient perchloroethylene concentrations data for nine states; the decline in California (88%) was steeper than for the other eight states (39%).<sup>81</sup> For a later period (2003–2010), however, the national decline<sup>19,82</sup> was similar to that found in this study. Figure 3c shows a steep decline in perchloroethylene concentrations until about 2004, consistent with concentrations declining earlier in California than in other states. Hexavalent chromium concentrations declined 33% (2005–2010) nationally,<sup>19,82</sup> compared to 53% for that period from this study, even though California's steepest declines occurred earlier: ARB regulations controlled emissions from plating facilities and cooling towers in the 1980s.

**Secondary TACs (Formaldehyde, Acetaldehyde).** For urban areas nationally, mean ambient formaldehyde concentrations declined 14% from 2003 to 2010, while acetaldehyde declined 17%.<sup>19,82</sup> This study shows similar declines for that period: 13% for formaldehyde, and 18% for acetaldehyde. The complexity of photochemical formation and removal processes for these TACs increases the difficulty in quantifying their expected ambient trends. Although these aldehyde declines are not as steep as for the other five TACs reviewed, they are steeper than the 7% decline in ozone (another secondary pollutant) in the western U.S. for 2001–2010.<sup>87</sup> Continued ambient declines for these aldehydes is anticipated as the emissions of their VOC precursors continue to decline.

**Evaluation of Cancer Risk.** Statewide cancer risks were determined using the calculated unit cancer risk factors (Table 1) and ambient statewide levels for each TAC, 1990–2012. Figure 4 shows a 76% decline in cumulative increased cancer risk per million people, from 1990 to 2012, due to inhalation of ambient air (caption notes interpolation for DPM and extrapolation for hexavalent chromium and aldehydes). This corresponds to a cumulative risk reduction from 3000 cancer cases per million residents in 1990 to 730 in 2012. This decline has been driven mostly by decreased exposure to DPM, followed by benzene and 1,3-butadiene. For 1990–2012, cancer



risk declined 68% for DPM, 89% for benzene, 88% for 1,3-butadiene, 94% for perchloroethylene; 88% for hexavalent chromium, 21% for formaldehyde, and 20% for acetaldehyde. As a percentage of the combined cancer risk from these seven TACs, the risk from these two aldehydes increased from 3.0% in 1990 to 9.7% in 2012.

Figure 4 shows that from 1990 through 1995, and again from 2003 through 2012, the statewide cancer risk from exposure to benzene was greater than to 1,3-butadiene; but from 1996 through 2002, the opposite was true. In 1996, RFG-2 required a steep reduction in the benzene content of gasoline, which refiners generally accomplished by hydrogenating benzene to cyclohexane, a 1,3-butadiene precursor.<sup>88,89</sup> This is consistent with the increase in cyclohexane in regular gasoline sold in the SFBA from 1.17 weight% in 1995 to 1.84% in 1996.<sup>90</sup> Subsequently, the cyclohexane content of gasoline declined,<sup>91</sup> because refiners found more cost-effective ways to lower the benzene content.<sup>92</sup>

In 1991, the ARB estimated that ambient exposure to perchloroethylene emissions from eight facilities resulted in up to 14 potential excess cancer cases in 5.5 million people.<sup>93</sup> The ARB's 2007 dry cleaning regulation is expected to reduce statewide risk to less than one cancer case per million by 2020.<sup>32</sup> Also, ambient monitoring (MATES-III) revealed high levels of hexavalent chromium that were traced to a cement facility in Riverside.<sup>46</sup> That finding led to controls that reduced its emissions and resultant exposures. These stationary-source TAC examples indicate that near-source residents may have especially benefited from TAC emission reductions.

In general, these ambient declines occurred earlier in California than elsewhere. Emission reductions and lower cancer risk correlate with emissions controls adopted in California, primarily controls on mobile sources and targeted stationary-source controls.

Further reductions in mobile source TAC emissions are expected from continuing efforts to improve fuel formulations, reduce vehicle exhaust emissions, and promote less polluting transportation modes. For stationary source TACs, perchloroethylene concentrations declined 90% and hexavalent chromium declined 86% (1990–2012); however regulatory controls probably led to even greater emission reductions, considering that California started regulating these TACs in the 1980s. Implementation of current control measures is expected to lead to further reductions in emissions for both TACs.

Most cancer risk from identified TACs is from DPM, and DPM concentrations represent a larger percentage (71%) of the overall cancer risk in 2012 than in earlier years. This is due to the earlier adoption of control measures for other TACs, and to the relatively long lifetime and slow turnover to cleaner technologies for diesel engines. However, the implementation of ARB's recent diesel engine retrofit and replacement requirements<sup>94</sup> has accelerated fleet turnover to cleaner trucks,<sup>26,57</sup> and significant additional reductions are projected statewide.<sup>56</sup>

The decreased exposure (from 1990 to 2012) to ambient concentrations of the seven TACs reviewed here resulted in a reduced cancer risk of thousands of fewer cancer cases per million exposed in California. Before 1990, air toxics regulations likely resulted in additional reductions in cancer risk, but these reductions are unquantified because they occurred prior to completion of California's air toxics monitoring network. Phased implementation of recent regulations is expected to

lead to further reductions in ambient TAC concentrations and cancer risk.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02766.

Figures and tables that are described above and a detailed methodology for DPM calculations (PDF)

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### Notes

The authors declare no competing financial interest.

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