Ambient Trends of Benzene in California from 1990 through 1995

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ABSTRACT

The California Air Resources Board has for the past six years maintained a routine, canister-based ambient toxics monitoring network in urban areas of California. The ambient record is now extensive enough to evaluate the trend of toxic pollutants within the State. This paper evaluates the trend in benzene at seventeen different sites in major population centers in California between 1990 and 1995. Even when considering measurement variability, a significant downward trend in ambient benzene concentrations has been observed throughout the State with an average reduction of 49 percent during the study period. The paper also presents emissions inventory trends of benzene for the same period whose reduction can be attributed to the vehicle emission controls and clean fuel programs.

INTRODUCTION

The California Air Resources Board (ARB) is required under the Toxic Air Contaminant Identification and Control Act (AB 1807-1983, amended AB 2728-1993) to identify and control toxic air contaminants. In 1985, the ARB established a twenty station toxics monitoring network within major urban areas to provide data to determine the average annual concentrations of toxic air contaminants as input to the identification process, and to assess the effectiveness of controls.[1] This paper presents an evaluation of the ambient trend for benzene in California using monitoring data obtained from that network.

Benzene has been identified as a human carcinogen and has been one of 19 gases measured by the ARB since the start of the toxics monitoring program. The ambient data have supported subsequent identification and control strategies for benzene. In California, the dominant source of benzene is motor vehicles, with emissions occurring from exhaust and evaporation processes. The trend analysis of the ambient benzene data has been performed for a six year study period (1990 through 1995) to gauge the aggregate success of the various control programs implemented during that time. The results of the ambient analysis are compared to inventory estimates to corroborate the benefits of recently enacted control efforts. Issues of variability and accuracy are also addressed to support the results.

MONITORING AND ANALYSIS

The Monitoring and Laboratory Division (MLD) is responsible for the field collection and laboratory analysis of the ambient samples for toxic air contaminants. Twenty monitoring sites were established at major population centers throughout the state for this purpose. Samples were collected over a 24-hour period every 12 days. Ambient air was drawn through a dedicated station probe with a low-volume gaseous sampler (Xontech Model 910A) into a whole air container. Samples prior to 1990 were collected in Tedlar bags. Since then, the collection has been with six-liter SUMMA® polished stainless

steel canisters. An extensive study indicated that treated canisters performed better than did Tedlar bags for retention of some volatile organic compounds. [2,3]

Samples were analyzed at the MLD Laboratory in Sacramento using state-of-the-art gas chromatography methods. The analysis method for benzene involves pre-concentration of an aliquot sample, then separation and detection by photoionization. The chromatogram peaks are identified by their characteristic retention times and quantified by reference to external standards. The analysis procedure and equipment used in the analysis of benzene were updated twice during the study period. A cross-check of each new system indicated that results for benzene had shifted during the study period of 1990 through 1995. This difference has been incorporated into the following analyzes.

QUALITY ASSURANCE

Accuracy

The laboratory gas chromatographic instruments used in the ambient toxics monitoring program are calibrated daily with standards containing the target compounds at concentrations that approximate the upper ambient concentration range. The calibration standards are produced and certified by the National Institute of Standards and Technology (NIST).[4] The mass flow controllers used during field sampling are certified by the MLD every six months using a NIST traceable flow standard.

Precision (collocated sampling)

The system variability (or total precision of data) of the ambient toxics program is measured by the variation derived from collocated samplers situated at three network stations. The collocated samples were treated similar to the primary samples with respect to sampling, transportation, and analysis procedures. The three collocated stations were located at Bakersfield in the San Joaquin Valley, Concord in the San Francisco Bay Area, and Rubidoux in the South Coast.

The system variability for each compound is defined as plus or minus two times the relative standard deviation as shown in Equation 1, where Equation 2 is used to estimate the standard deviation (**s**).[5] The system variability value represents the range in which there is a 95 percent probability that the true average value will reside.

Equation (1) **System Variability** = $\pm$ 2 * [(**s** / average concentration) * 100],

Equation (2) $\mathbf{s} = [\ \Sigma\ (\text{difference among pair})^2\ /\ 2 * (\text{number of pairs})]^{1/2}$

Only samples whose reported concentrations were above the detection limit were used in the precision calculations. Between 1990 and 1995, 395 collocated sample pairs were obtained to estimate precision. The system variability for benzene is calculated to be 21 percent using Equations 1 and 2. The results of regression analysis indicates that the regular and collocated paired values are in excellent agreement (slope = 0.97, regression coefficient = 0.98, intercept = 0.04, with an average concentration = 1.85). The system variability and correlation results are quite good given that they represent the collection and analysis components of the final determination. The three collocated sites represent different regions, average concentrations, and site operators. Thus, the average system variability value of the collocated sites is representative of all the network sites. A directional trend can be detected if ambient concentrations exceed the upper or lower 21 percent limit.

DATA COMPLETENESS AND TREATMENT

During the study period, 17 of the 20 network sites remained in continuous operation. Samples were collected on a 1-in-12 day sampling schedule. This schedule resulted in approximately 7 to 8 samples per quarter for each site. An evaluation of the data completeness showed 96 percent of the quarterly averages contained 6 to 10 samples with no obvious site or seasonal bias noted. Therefore, the benzene database was considered complete and representative of urban California.

In the original database, samples below the Limit of Detection (LOD) for benzene (0.5 ppb) were reported as "less than the LOD." For this study, all values reported as "less than LOD" were reassigned a value of 0.2, or approximately one-half the LOD. Benzene samples obtained between January 1993 and December 1995 were increased to be consistent with the results of a change in the analytical method ($y= 0.86x - 0.23$).[6]

RESULTS

Ambient Benzene Concentration

The study period for this analysis is from January 1, 1990, to December 31, 1995. It includes only samples collected using stainless steel canisters. Quarterly averages were calculated using data from the 1-in-12 day sampling schedule. Annual ambient benzene averages were derived from the complete quarterly averages and are summarized in Table 1. The data show a downward trend exceeding the method variability of 21 percent in statewide benzene concentration for the six year study period.

Linear regression analysis was used to evaluate the estimated reduction. The linear regression line is expressed below as Equation 3.

Equation (3) $\mathbf{y = mx + b}$, where m is the slope of the line, and b is the y-intercept

The analysis using quarterly benzene averages was performed on data from 17 monitoring stations that operated continuously during the study period. A graphical representation of results from the Los Angeles site is presented as Figure 1. The winter months at a majority of the sites show higher concentration than the summer months. The quarterly averages above the best fit line generally represent the fall and winter quarters and those below the line are typically spring and summer quarters. A five year subset of the six year study period was used for the quarterly regression analysis. The same beginning and ending quarter (third quarter) was chosen for the analysis to reduce seasonal bias. The statewide decline in benzene concentration was 49 percent during the five year period (third quarter 1990 through third quarter 1995). The five year percent reduction in ambient benzene levels for each site is summarized in Table 2, and ranges from 35 percent at Rubidoux and Richmond to as high as 68 percent in Fresno and Santa Barbara. In general, the results of the analyses summarized in Tables 1 and 2 corroborate a significant downward trend for benzene concentration at all sites. Further, we find that with increasing frequency, individual benzene values are reported at or below LOD (0.5 ppb), a level that still poses a significant health risk.

Summer and Winter Trends

Given the distinct seasonal nature of benzene levels, a separate analysis to evaluate the trends as a function of the season was performed on the same data from the 17 monitoring stations. For this, the summer season was defined as July through September and the winter from December through February. The graphical representation of the differences in the overall trend by season at the Fresno site (Figure 2) shows a greater rate of reduction during the winter seasons when compared to the summer. The reduction in benzene during a five year period at Fresno was 63 percent during the winter periods, and 26 percent during the summer periods. The pattern of greater reductions occurring during the winter was repeated in varying degrees at 13 of the 17 sites, with sites in Southern California tending to report comparable seasonal reduction rates. The percent values for the rates of summer and winter period decline are summarized for all sites in Table 2. Further study would be required to better understand the causes of the observed difference between summer and winter rates of reduction.

Emissions Inventory

Inventory estimates of benzene can be used to corroborate the directional trend of ambient benzene. On-road mobile sources are estimated to have contributed two-thirds of the benzene emissions over the study period, with other mobile, area, and point sources contributing the remainer.[7] Total benzene emissions have steadily declined from 1990 to 1995, mostly as a result of reductions from on-road mobile sources. [7] Two major categories of emission controls affecting the on-road mobile inventory estimates were the ARB's low emissions vehicle program [8] (beginning with the 1994 model year), and the State and Federal programs to reduce emissions of volatile organic compounds (VOCs) and/or benzene from fuels.

Figures 3 and 4 illustrate statewide ambient benzene concentrations and the estimated benzene emissions from on-road sources over the study period, respectively. [9,10] A comparison of the two figures shows the same directional trends. In Figure 4, specific State and Federal fuel regulatory programs that affect the benzene content of fuel are shown on the time-line.[11] Although early fuel regulatory controls focused on reducing VOCs to reduce ambient ozone levels, they had a secondary effect of limiting benzene emissions. Current fuel regulations have specifically targeted benzene in addition to VOCs. The programs contributing to the reduction of ARB's benzene inventory estimate include:

- ARB California Phase I gasoline (January 1992) - Regulation required lower Reid Vapor Pressure (RVP) or volatility of gasoline in the summer months, which effectively limited evaporative emissions of all gasoline component including benzene.

- ARB Winter component of California Phase 1 gasoline (October 1992) - Regulation required that that fuel sold in the winter months contain oxygenated compounds (e.g., methyl t-butyl ether). The purpose of the oxygenated fuel was to limit carbon monoxide emissions; however, it has a secondary effect of limiting VOCs emissions.

- ARB clean diesel fuel (October 1993) - Regulation required that diesel fuel sold in California be limited in sulfur and aromatic content. Benzene is an aromatic compound.

- U.S. EPA Federal Phase 1 gasoline (January 1995) - Regulation requires gasoline sold in the high ozone areas to have lower volatility, contain oxygenated compounds, and specifically limit the benzene content in the fuel. In California, the regulation applies to large populated regions in the southern portion of the state.

- ARB California Phase 2 gasoline or "Cleaner Burning Gasoline" (June 1996) - Regulations specifies limits on eight properties of gasoline including a direct limit on benzene content. Although the regulation begins in April 1996, some refineries have produced and sold gasoline that meets Phase 2 specifications since the end of 1995. [11]

CONCLUSIONS

Based on the review of ambient benzene data for the study period, we conclude that:

- A consistent downward trend in ambient benzene concentrations occurred at each site between 1990 and 1995. The statewide reduction was approximately 49 percent.

- Seasonal trends exist with winter concentrations generally higher than summer concentrations.

- The rate of decrease in ambient benzene concentration is greater in winter than summer at 13 of 17 sites.

- Ambient benzene data reflect emissions controls attributed largely to controls in vehicles and in-use fuels.

- Current laboratory analytical techniques will need to be improved to measure lower ambient benzene concentrations.

ACKNOWLEDGMENTS

The monitoring and analysis of the toxics program is sponsored by the Monitoring Laboratory Division of ARB under the general direction of William V. Loscutoff, Chief. The monitoring stations are operated and maintained by Bill Oslund and his staff of the Air Quality Surveillance Branch. Michael Poore with George Lew and their laboratory staff analyzed the canister samples during the study period. Quality Management and Operations Support for the Program is provided by Jeff Cook and his staff. Jeff Cook and Dale Secord reviewed and provided comments for this paper. In addition, the author wishes to express appreciation to Dennis Goodenow and Chris Nguyen of the Technical Support Division (TSD) for providing emissions inventory estimates along with Michael Redgrave of TSD for the toxics database.

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Table 1. Annual Ambient Benzene Concentrations for California*

Air Basin	Sites	1990	1991	1992	1993	1994	1995
San Francisco Bay	**Concord**	1.9	1.8	1.5	1.2	1.1	1.1
	Fremont	2.1	1.8	1.3	1.4	1.3	1.3
	Richmond	2.3	2.1	1.6	1.8	1.7	1.5
	San Francisco	1.9	1.7	1.3	1.4	1.1	1.0
	San Jose	3.4	2.7	2.2	2.2	2.1	1.7
San Joaquin Valley	**Bakersfield-1**	3.0	2.4	1.7	1.6	C	-
	Bakersfield-2	-	-	-	-	O	1.2
	Fresno	2.4	2.7	1.5	1.5	1.5	1.4
	Modesto	2.4	2.1	1.3	1.4	1.1	1.3
	Stockton	2.1	2.1	1.5	1.3	1.2	1.1
Sacramento Valley	**Chico-1**	2.0	2.0	C	-	-	-
	Chico-2	-	-	O	1.1	1.2	0.9
	Citrus Heights	2.2	2.0	1.6	C	-	-
	Roseville	-	-	-	O	1.0	0.8
South Coast	**Burbank**	5.4	4.4	3.8	2.8	3.6	2.6
	Long Beach	3.9	2.6	2.8	2.0	2.1	1.7
	Los Angeles	3.9	3.5	3.2	2.5	2.7	2.3
	Rubidoux	2.7	2.3	2.0	1.8	2.0	1.5
	Upland	2.8	2.8	2.2	2.0	2.2	1.7
South Central Coast	**Santa Barbara**	3.0	2.1	1.5	1.2	1.4	0.9
	Simi Valley	2.2	1.6	1.3	0.9	1.1	0.8
San Diego	**Chula Vista**	2.2	1.2	1.1	0.8	1.1	0.8
	El Cajon	2.8	2.3	2.1	1.5	1.8	1.1
Average		2.7	2.3	1.9	1.6	1.6	1.3

***** (LOD = 0.2, '93-'95 increased to account for methods change (adjusted value = [0.23 + value] / 0.86).
Annual average calculated by averaging the quarterly averages.
O-opened station, C-closed station.

Table 2. Benzene Reduction in California 1990-1995*

Air Basin	Site	Percent Reduction: All Quarters	Winter	Summer	Ratio of Percent Reduction Winter / Summer
San Francisco Bay	**Concord**	55	64	25	2.5
	Fremont	39	60	-4	-
	Richmond	35	47	-4	-
	San Francisco	49	45	31	1.5
	San Jose	44	58	-7	
San Joaquin Valley	**Fresno**	68	63	26	2.4
	Modesto	59	68	21	3.2
	Stockton	56	58	24	2.4
South Coast	**Burbank**	49	51	14	3.7
	Los Angeles	38	30	20	1.5
	Long Beach	48	39	42	0.9
	Rubidoux	35	26	31	0.8
	Upland	37	30	25	1.2
South Central Coast	**Santa Barbara**	68	71	61	1.2
	Simi Valley	53	51	48	1.1
San Diego	**Chula Vista**	51	46	58	0.8
	El Cajon	54	54	38	1.4
Average		49	51	26	-

*Note : Winter and Summer are not aligned with calendar quarters. Quarterly regressions were calculated using quarter averages for 3rd quarter 1990 through 3rd quarter 1995. Winter regressions were calculated using winter averages (December, January, and February) for the 1990-91 through the 1994-95 winter. Summer regressions were calculated using summer averages (July, August, and September) for the 1990 through 1995 summers.

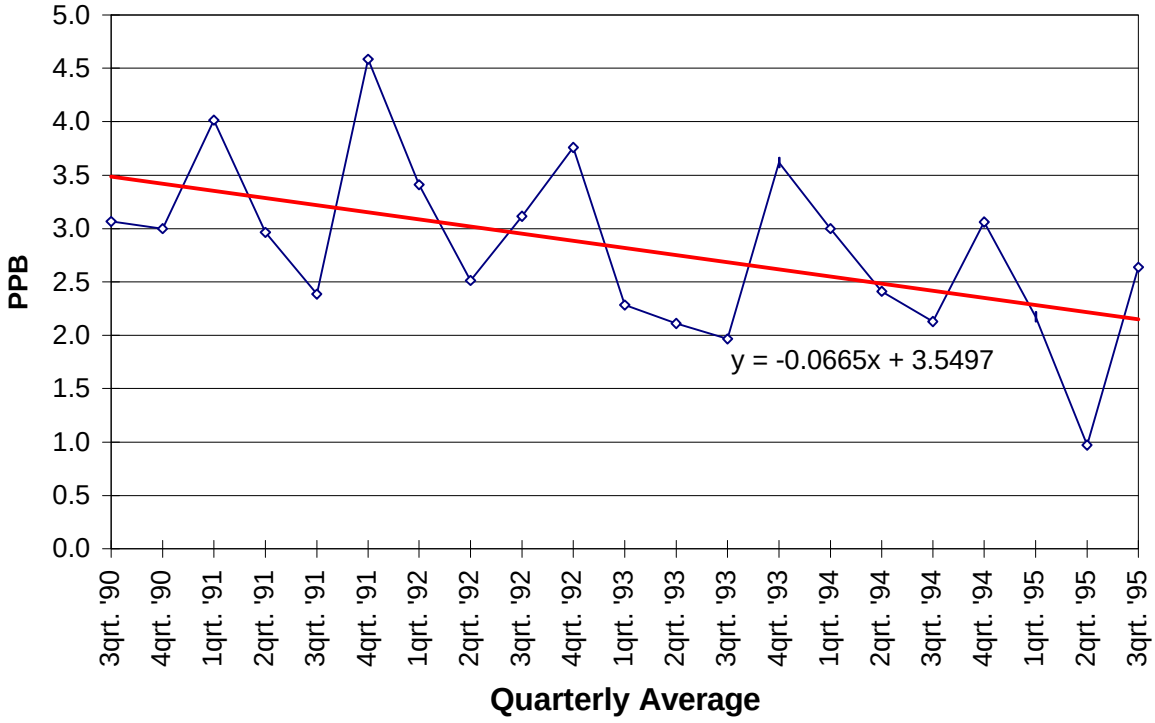

Figure 1. Ambient Benzene Trend at Los Angeles

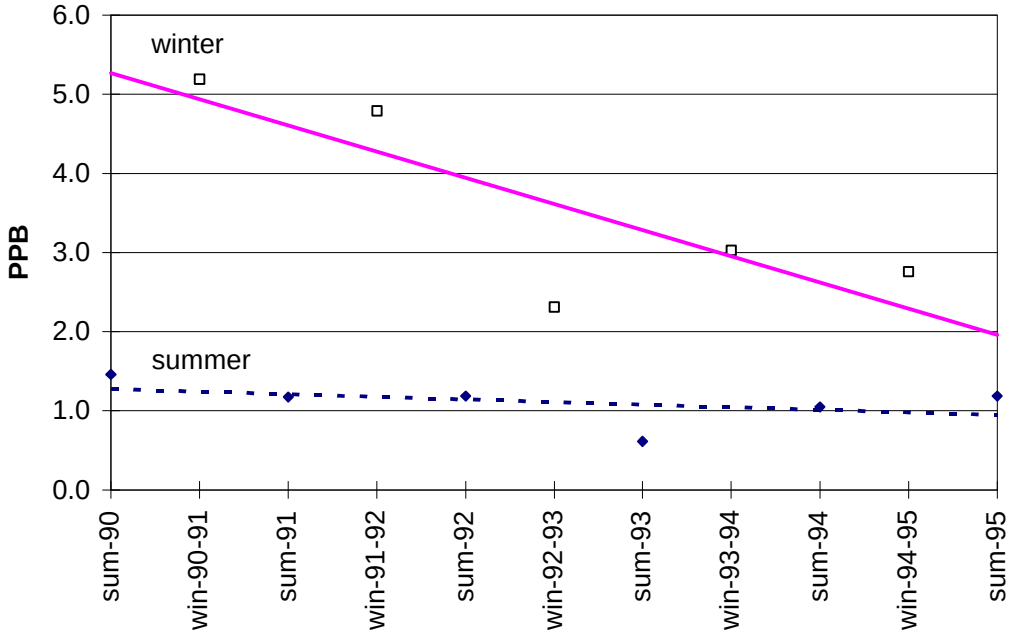

Figure 2. Seasonal Benzene Trend at Fresno

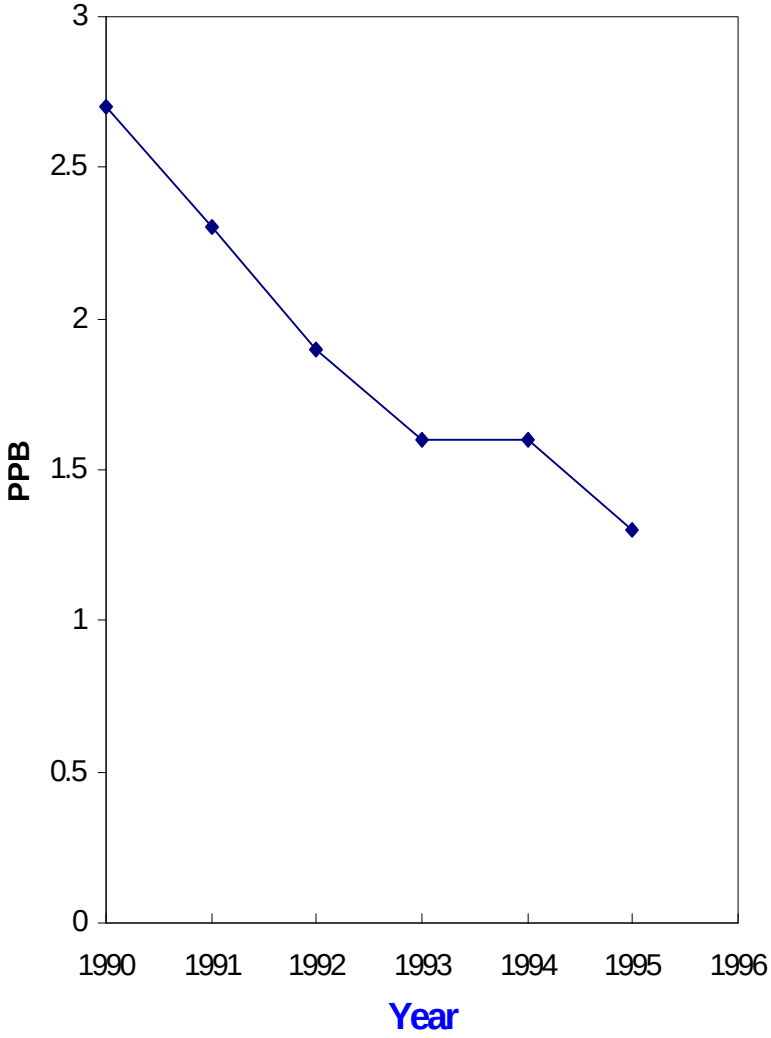

Figure 3. Statewide Ambient Benzene

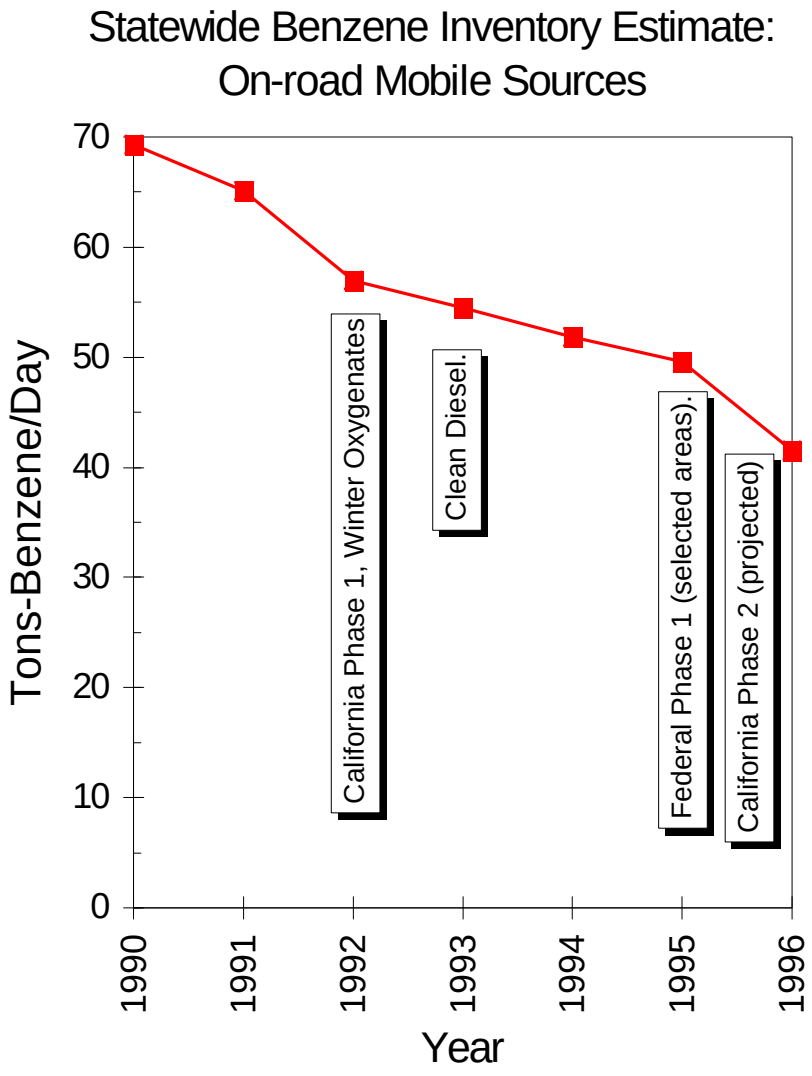

Figure 4. Inventory Estimate