California Environmental Protection Agency

Air Resources Board

Technical Support Document

Proposed Identification of 1,3-Butadiene

as a Toxic Air Contaminant

Part A
Exposure Assessment

State of California
Air Resources Board
Stationary Source Division

May 1992

BOARD VERSION

REPORT TO THE AIR RESOURCES BOARD ON THE PROPOSED IDENTIFICATION OF 1,3-BUTADIENE AS A TOXIC AIR CONTAMINANT

"PART A" TECHNICAL SUPPORT DOCUMENT
PUBLIC EXPOSURE TO, SOURCES AND EMISSIONS OF
1,3-BUTADIENE IN CALIFORNIA

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BOARD VERSION
REPORT TO THE AIR RESOURCES BOARD ON 1,3-BUTADIENE

Part A - Public Exposure To, Sources and Emissions of Atmospheric 1,3-Butadiene in California

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I.
INTRODUCTION

According to Section 39655 of the California Health and Safety Code, a toxic air contaminant (TAC) is "... an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health." This report, Part A of the Technical Support Document Proposed Identification of 1,3-Butadiene as a Toxic Air Contaminant, prepared by the staff of the California Environmental Protection Agency's (Cal/EPA) Air Resources Board (ARB), is an evaluation of the compound's emissions, ambient (outdoor) and indoor concentrations, statewide population exposure, and atmospheric persistence and fate. The Part B report, prepared by the staff of the Cal/EPA's Office of Environmental Health Hazard Assessment (OEHHA), assesses the health effects of 1,3-butadiene. The ARB will consider the Technical Support Document, the findings of the Scientific Review Panel (SRP), written comments, and public testimony to determine if 1,3-butadiene should be identified as a TAC.

A. SUMMARY OF CALIFORNIA HEALTH AND SAFETY CODE SECTIONS 39660-39662 (IDENTIFICATION OF TOXIC AIR CONTAMINANTS)

Section 39650 (f) of the California Health and Safety Code requires the use of the following criteria for prioritizing substances for evaluation as possible toxic air contaminants: 1) risk of harm to public health, 2) amount or potential amount of emissions, 3) manner of usage, 4) persistence in the atmosphere and, 5) ambient concentrations.

Once a substance is selected to enter the TAC identification process, the ARB requests relevant information from the public and a written evaluation of available health effects information (Part B) from the OEHHA. The OEHHA staff's evaluation is required to contain an estimate of the threshold exposure level above which the compound causes or contributes to adverse health effects. In the case where no threshold of significant adverse health effects can be determined, the OEHHA is required to state the range of risk to humans resulting from current or anticipated exposure.

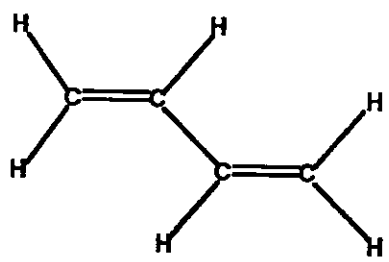
Simultaneous with the preparation of the OEHHA health evaluation, the ARB staff prepares an exposure assessment (Part A) including information on the substance's usage, emissions or potential emissions, environmental persistence, and available outdoor and indoor exposure levels.

Following a public comment period, the Staff Report/Executive Summary and Parts A, B, and C (the public comments and staff responses document) are formally reviewed by the SRP at a public meeting. Upon reviewing the data, assessments, and conclusions of the report and ascertaining that appropriate scientific methods were used to gather and analyze the data presented, the SRP submits written findings to the ARB (the Board). At a public hearing, the Board decides whether or not the evidence in the Technical Support Document supports the identification of a substance as a toxic air contaminant, and if so, whether there is evidence of a threshold exposure below which adverse effects are not expected to occur. Once a substance is identified as a TAC and listed in Section 93000 of Title 17 of the California Code of Regulations, the ARB staff prepares a report on the need and appropriate degree of regulation pursuant to Sections 39665-39668 of the Health and Safety Code.

B. 1,3-BUTADIENE AS A CHEMICAL COMPOUND

1,3-Butadiene is an unsaturated aliphatic hydrocarbon containing two double bonds. It has the chemical formula C_4H_6 (Figure I-1), and is also known as bivinyl, divinyl, α,γ-butadiene, erythrene, vinylethylene, biethylene and pyrrolylene.

Figure I-1
Structure of 1,3-Butadiene



The majority of California's ambient (outdoor air) emissions of 1,3-butadiene are the result of the incomplete combustion of gasoline and diesel fuels. The ARB staff estimates that approximately 3,900 tons of 1,3-butadiene are emitted annually into California's air.

II.

PHYSICAL AND CHEMICAL PROPERTIES OF 1,3-BUTADIENE

At room temperature, 1,3-butadiene is a flammable, colorless gas with a pungent, aromatic odor. It is insoluble in water, slightly soluble in methanol and ethanol, and soluble in organic solvents such as benzene and ether (US EPA, 1989). 1,3-Butadiene is not known to contribute to either global warming or to the depletion of stratospheric ozone. Some of the physical and chemical properties of 1,3-butadiene are shown in Table II-1.

Table II-1
Physical and Chemical Properties of 1,3-Butadiene

Property	Value	Reference
Boiling Point	- 4.5° C	Merck Index, 1983
Density (20° C)	0.6211 g/cm^3	US EPA, 1989
Melting Point	- 108.91° C	US EPA, 1989
Molecular Weight	54.09 g/mole	Merck Index, 1983
Vapor Pressure (15.3° C)	2.0 atm	US EPA, 1989
Conversions (25° C)		
1 ppb (by volume)= 2.21 μg/m^3		
1 μg/m^3 = 0.45 ppb (by volume)		

Most of the 1,3-butadiene emitted to California's atmosphere is a result of the incomplete combustion of gasoline and diesel fuel in motor vehicles. During combustion of the fuel, 1,3-butadiene is expected to be formed primarily by hydrogen atom abstraction from a saturated carbon atom on a straight-chain alkene. Dryer and Brezinsky (1986) have shown that 1,3-butadiene is a significant intermediate oxidation product of n-octane, while Venkat et al. (1982) have shown that butadiene is present as an intermediate in the oxidation of the fuel components benzene, toluene, and ethylbenzene.

References for Chapter II

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US EPA, 1989. Locating and Estimating Air Emissions from Sources of 1,3-Butadiene. EPA-450/2-89-021, December 1989

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III.

PRODUCTION, USES, AND EMISSIONS OF 1,3-BUTADIENE

1,3-Butadiene is not commercially produced in California, although it is commercially produced elsewhere in the United States. The largest national uses of 1,3-butadiene include the production of synthetic elastomers and adiponitrile.

In California, the majority of 1,3-butadiene emissions are the result of the incomplete combustion of gasoline and diesel fuels by mobile sources. Mobile sources account for approximately 96 percent (3,700 tons, see Table III-1) of the total annual emissions statewide (approximately 3,900 tons) for quantified sources. Stationary point and area sources also emit 1,3-butadiene during fuel combustion. Stationary point sources emit 1,3-butadiene from boilers, heaters, internal combustion engines, and turbines, while stationary area sources emit 1,3-butadiene during agricultural processes, oil and gas production, manufacturing and industrial processes, service and commerce, and residential fuel combustion.

Non-combustion emissions of 1,3-butadiene occur during vehicle tire wear, petroleum refining, and styrene-butadiene copolymer production.

A. PRODUCTION OF 1,3-BUTADIENE

1,3-Butadiene is commercially produced in the United States through one of two methods. The first is the recovery of 1,3-butadiene during ethylene production (from a C_4 hydrocarbon stream). The second process involves the oxidative dehydrogenation of n-butenes. Almost all of the 1,3-butadiene produced in the United States involves the first method. There are no commercial producers of 1,3-butadiene in California (US EPA, 1989). For U.S. production, import, export, and usage of 1,3-butadiene, see Figure III-1.

Table III-1
1,3-Butadiene Emission Inventory[a]

Source Type	Emissions (Tons/Year)	Inventory Year
Mobile Sources		
On-Road Vehicle Fuel Combustion	2,600	1990
Other Mobile Source Fuel Combustion	1,100	1987
Tire Wear	Not Available	
Stationary Area Sources		
Fuel Combustion	110	1987
Stationary Point Sources		
Fuel Combustion	35	1988
Petroleum Refining	9	1989
Styrene-Butadiene Copolymer Production	1.5[b]	1991
Acrylonitrile-Butadiene-Styrene Resin Production	None[c] Expected	1988
Chemical Production	None[c] Expected	
Approximate Total of[d] Identified Emissions:	3,900 TPY	

Notes:

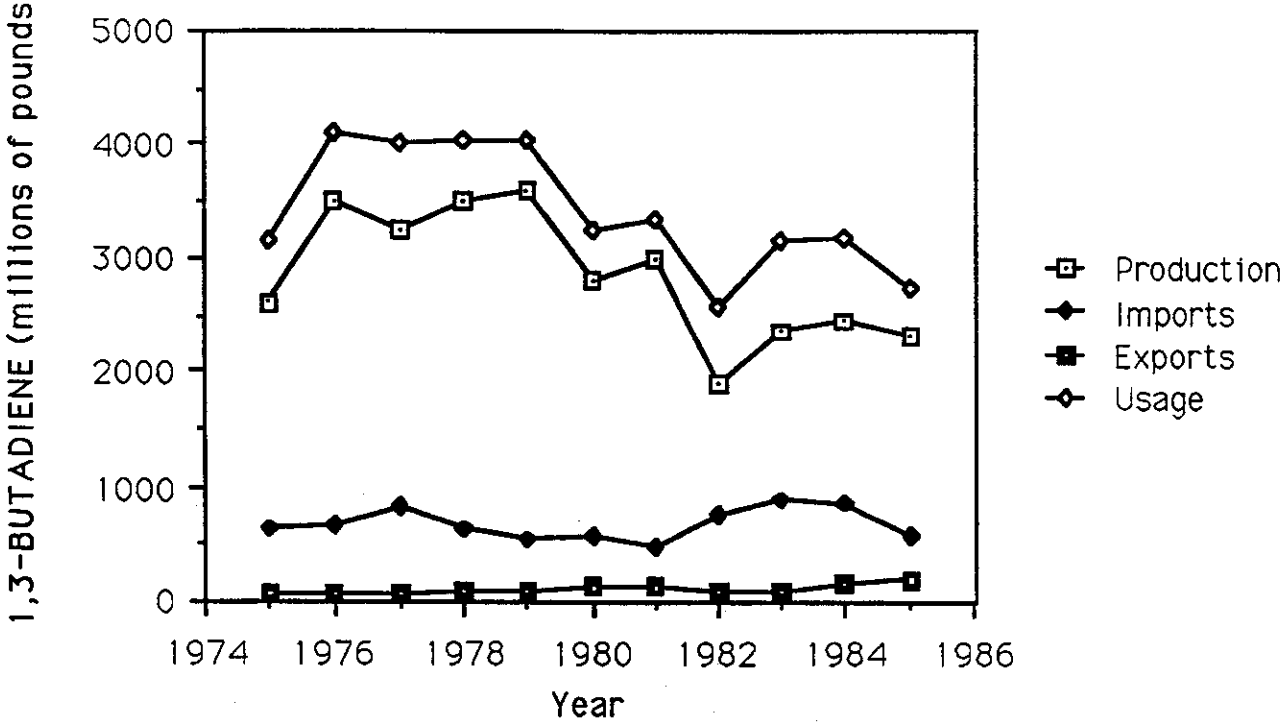
a. Additional emissions will result from unidentified sources and from sources for which emissions have not been estimated (e.g., tire wear).

b. The estimate does not include emissions from the Southern California facility due to a lack of reported data.

c. See text for explanation.

d. The total is not the same as the sum of the emissions due to rounding.

Figure III-1
U.S. Production, Imports, Exports, and Use of 1,3-Butadiene



B. USES OF 1,3-BUTADIENE

The largest use of 1,3-butadiene in the United States is in the production of synthetic elastomers, which include: styrene-butadiene copolymer (SB), acrylonitrile-butadiene-styrene resin (ABS), polybutadiene, neoprene, and nitrile rubber. There are no polybutadiene, neoprene, or nitrile rubber production facilities in California (US EPA, 1989). The US EPA (1989) reports that there are two SB copolymer production facilities and one ABS resin production facility in California.

The second major national use of 1,3-butadiene is in the production of adiponitrile, the raw material used in nylon 6,6 production. Nylon 6,6 is highly resistant to common solvents, alkalis, heat, and impact, and is used to make light weight gears and a number of mechanical parts. The US EPA (1989) reports that there are no adiponitrile production facilities in California.

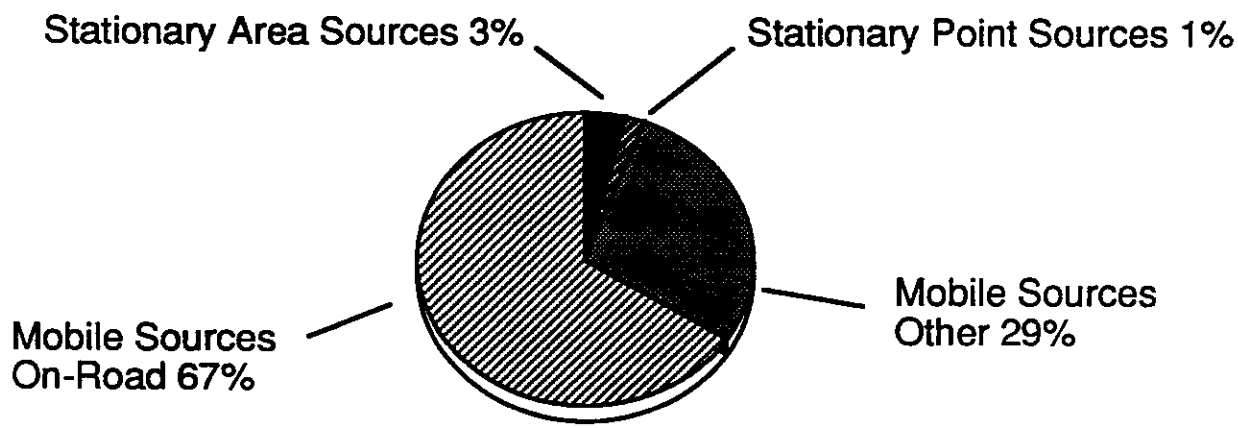
C. EMISSIONS OF 1,3-BUTADIENE

There are approximately 3,900 tons of 1,3-butadiene from quantified sources emitted into California's air each year (see Table III-1). The majority of these emissions are the result of incomplete combustion of

petroleum-derived fuels, rather than the escape of 1,3-butadiene during a chemical manufacturing process.

An estimated 96 percent of California's 1,3-butadiene emissions are the result of the combustion of gasoline and diesel fuels by mobile sources. "On-road" and "other" mobile sources account for 67 percent (2,600 tons) and 29 percent (1,100 tons), respectively, of the total annual statewide estimate of 1,3-butadiene emissions from quantified sources (see Figure III-2).

Figure III-2
California Emissions of 1,3-Butadiene



"Stationary area" sources of fuel combustion account for approximately 3 percent (110 tons) of the total annual statewide estimate of 1,3-butadiene emissions from quantified sources (see Figure III-2).

"Stationary point" sources account for approximately 1 percent (45.5 tons) of the total annual estimate of 1,3-butadiene emissions in California from quantified sources (see Figure III-2). Stationary point sources emit 1,3-butadiene during fuel combustion, petroleum refining, and styrene-butadiene copolymer production.

1. <u>Mobile Sources</u>

Mobile sources account for approximately 96 percent (3,700 tons) of annual 1,3-butadiene emissions. This estimate includes fuel combustion emissions from both on-road vehicles and other mobile sources. Tire wear is also a source of 1,3-butadiene emissions, but is not included in this estimate due to the lack of data.

Mobile sources emit 1,3-butadiene as a result of the incomplete combustion of gasoline or diesel fuel. 1,3-Butadiene emissions increase roughly proportionately to hydrocarbon emissions in engine exhaust.

According to the United States Environmental Protection Agency (US EPA), refineries attempt to minimize the 1,3-butadiene content of gasoline and diesel fuels because the combustion of 1,3-butadiene can cause varnish to form in the engine. Because of the insignificant amount of 1,3-butadiene present in fuel, the US EPA assumes that there will be no 1,3-butadiene emissions from refueling operations or fuel evaporation (US EPA, 1989).

a. On-Road Motor Vehicles

California's on-road motor vehicles emitted approximately 2,600 tons of 1,3-butadiene during 1990 (see Appendix A). On-road motor vehicles include motorcycles, light-duty passenger vehicles, and light-, medium-, and heavy-duty trucks. Emission factors developed for this category were based on data which included 1988 and 1989 model-year vehicles; therefore, the staff estimated 1,3-butadiene emissions using the most recent available activity data (i.e., inventory year 1990). Emission estimates are based on the emission factors, expressed in weight percent of 1,3-butadiene to total organic gases (TOG), and the TOG emissions from individual vehicular classes (ARB, 1990; ARB, 1991a).

Many of California's on-road motor vehicles are equipped with catalysts to reduce exhaust emissions of hydrocarbons (e.g., 1,3-butadiene). Vehicles that are not equipped with functioning catalysts emit far greater amounts of 1,3-butadiene than do vehicles with functioning catalysts. In California, catalyzed vehicles account for approximately 86 percent of the on-road vehicle miles traveled, but are only responsible for an estimated 46 percent of the on-road vehicle fleet's total emissions of 1,3-butadiene (see Appendix A). Uncatalyzed on-road vehicles, accounting for only 14 percent of the on-road vehicle miles traveled, are responsible for approximately 54 percent of the on-road vehicle emissions of 1,3-butadiene. Also, much of the 1,3-butadiene emitted from catalyzed vehicles is emitted when the catalyst is still cool; once the catalyst has reached operating temperature, it dramatically reduces the amount of emitted 1,3-butadiene.

b. **Other Mobile Sources**

California's emissions of 1,3-butadiene from "other" mobile sources are approximately 1,100 tons per year (see Appendix A). This category includes off-road vehicles, boats, trains, ships, aircraft, mobile equipment and utility equipment. Engines in this group are rarely catalyzed for reduction of hydrocarbon exhaust emissions (e.g., 1,3-butadiene); uncatalyzed engines emit far greater amounts of 1,3-butadiene than engines with functioning catalysts. Emission factors for on-road diesel- and gasoline-powered vehicles were assumed to be applicable to similar vehicles and equipment in the "other mobile source" category, and were used to estimate emissions for this category. The 1,3-butadiene emission estimates for this category are based on the 1987 inventory year because 1987 represents the most recent available activity data (ARB 1989a; ARB 1991b).

c. **Tire Wear**

Most of the styrene-butadiene rubber and polybutadiene produced in the United States is used to manufacture tires and tire products. 1,3-Butadiene is released to the atmosphere as the tire wears on the pavement. There is not enough information to develop an emission estimate at this time and thus, emissions from tire wear have not been quantified.

2. <u>Stationary Point Sources</u>

Stationary point sources also have significant emissions, a specific location, and are separately reported from the mobile source inventory. Stationary point sources emit 1,3-butadiene during fuel combustion, petroleum refining, styrene-butadiene copolymer production, acrylonitrile-butadiene-styrene resin production, and chemical production.

The staff estimates statewide emissions of 1,3-butadiene from stationary point sources to be approximately 46 tons per year.

a. **Fuel Combustion**

Combustion sources emit 1,3-butadiene as a result of the incomplete combustion of the fuel similar to the processes associated with motor vehicle exhaust. Sources of fuel combustion include (but are not limited to) boilers, heaters, internal combustion engines, and turbines. The staff estimates statewide emissions of 1,3-butadiene from fuel combustion sources to be

approximately 35 tons per year (see Appendix A). This estimate is based on the TOG emissions from different types of combustion fuels (ARB, 1989c), speciation profiles, and emission rates of 1,3-butadiene.

b. Petroleum Refining

The Oil & Gas Journal lists 31 petroleum refining facilities in California (Oil & Gas, 1989). Of these facilities, there are 5 facilities in the Bay Area Air Quality Management District for which 1,3-butadiene emissions data are available (BAAQMD, 1989a). Using these data and the design capacities of all 31 refineries to process crude oil, the staff estimates air emissions of 1,3-butadiene from petroleum refining processes statewide to be approximately 9 tons per year (see Appendix A).

c. Styrene-Butadiene Copolymer Production

Styrene-butadiene (SB) copolymers are made up of giant molecules formed by the union of simple molecules of styrene and 1,3-butadiene. SB copolymers can be either solid or an elastomer emulsion, depending on the composition and the extent of drying in the process.

The two types of solid copolymers are styrene-butadiene rubber and styrene-butadiene elastomer. Styrene-butadiene rubber typically contains more than 45 percent 1,3-butadiene, while styrene-butadiene elastomer typically contains more styrene. Emissions for both these types of solid SB copolymers are not differentiated. Solid SB copolymers are commonly used in tires, tire products, and mechanical rubber goods.

Elastomer emulsion SB copolymer is commonly referred to as styrene-butadiene latex. The emulsion process is the same process used for solid SB copolymers except that the emulsion breaking (coagulation) and drying steps are omitted. Latex is commonly used in foam products, carpet and textile backing, paper coatings, and adhesives.

There are two latex production facilities in California (one in Northern California and one in Southern California), and no solid SB copolymer production facilities. In 1984, the Northern California facility and its four affiliate facilities (located in other states) had a combined capacity to produce 175,000 megagrams (192,900 tons) of latex per year. In 1984 the

Southern California facility had the capacity to produce 25,000 megagrams (27,560 tons) of latex per year (US EPA, 1989).

Emission information reported to the Bay Area Air Quality Management District show that the Northern California facility is estimated to emit approximately 1.5 tons of 1,3-butadiene per year. Approximately 2,555 pounds of the 1,3-butadiene emissions came from the latex process and tank leaks, while an estimated 533 pounds of the 1,3-butadiene emissions came from equipment leaks. There are no available data to estimate emissions from the Southern California facility at this time, thus, the statewide emission estimate only includes emissions from the Northern California facility.

d. Acrylonitrile-Butadiene-Styrene Resin Production

Acrylonitrile-butadiene-styrene (ABS) resins are used to make a variety of plastic components including: automotive parts, pipes and fittings, appliances, electronics, business machines, telecommunications, construction, toys, recreational products, and plastic modifiers (US EPA, 1989). There are nine facilities in the United States producing ABS resins. At least five of these facilities use polybutadiene instead of 1,3-butadiene.

The only facility producing ABS resins in California is in Southern California. This facility had the capacity (in 1988) to produce 32,000 megagrams (35,000 tons) of resin per year, using polybutadiene as the raw material for ABS production. According to the US EPA, no 1,3-butadiene emissions are expected from ABS resins production using polybutadiene as a feedstock (US EPA, 1989). Thus, there are no 1,3-butadiene emissions expected from ABS resins production facilities in California.

e. Miscellaneous Uses of 1,3-Butadiene in Chemical Production

There are at least 20 facilities nationwide producing chemical products from 1,3-butadiene. According to the US EPA, a northern California chemical production facility is the only facility in California holding a permit to manufacture a chemical product from 1,3-butadiene (US EPA, 1989). The product is a fungicide; it is produced in a pressurized system which is vented to an incinerator on a continuous basis. The facility has not produced the fungicide since 1987 (BAAQMD, 1989b). Presently there are believed to be no 1,3-butadiene emissions from the production of fungicide in California.

3. Stationary Area Sources

Stationary area sources individually emit small amounts of 1,3-butadiene, but collectively result in significant emissions and are reported separately from either the point source or the mobile source inventory.

1,3-Butadiene emissions occur when stationary area sources combust petroleum-derived fuel (1,3-butadiene is a product of incomplete combustion). Area sources include agricultural activities, oil and gas production facilities, manufacturing and industrial sources, services and commerce, and residential fuel combustion. Based on TOG emissions from different fuel combustion sources (ARB, 1989a) and 1,3-butadiene emission rates, the staff estimates statewide 1,3-butadiene emissions to be approximately 110 tons per year from area sources of fuel combustion (see Appendix A).

D. EMISSION PROJECTION

Approximately 96 percent of California's outdoor 1,3-butadiene comes from mobile sources (both on-road motor vehicles and other mobile sources). Based on data from the ARB's emission factor and emission inventory models (EMFAC7EP and BURDEN7C) and estimates of emissions from other mobile sources, total organic gas exhaust emissions from California's mobile sources (the basis of the 1,3-butadiene estimate) are expected to steadily decrease through the year 2010. These decreases are a result of motor vehicle regulations that have already been implemented, and regulations that have been adopted and have future implementation dates.

Vehicles now sold in California are required to meet a standard of 0.39 grams per mile of non-methane organic gas. Starting in 1993, 40 percent of the new light-duty passenger vehicle fleet must meet a standard of 0.25 grams per mile; in 1994, 80 percent; and by 1995, 100 percent of the light-duty passenger vehicle fleet must meet the 0.25 grams per mile standard for non-methane organic gas. A 1990 ARB regulation ("Low-Emission vehicles/ Clean Fuels") will result in reductions in non-methane organic gases from light-duty and medium-duty vehicles by requiring a growing percentage of the new vehicle fleet to meet "low emission vehicle" standards through compliance options that include the use of "clean fuels" (e.g., compressed natural gas). This program will be "phased in" over the period 1994 through 2003.

The ARB's 1991 "Phase 2" reformulated gasoline regulations include a comprehensive set of standards which will affect eight gasoline properties, including: Reid vapor pressure, aromatic hydrocarbon content, oxygen content, benzene content, olefin content, sulfur content, T90 distillation temperature (the temperature at which 90 percent of a given volume of gasoline would evaporate), and T50 distillation temperature. Use of reformulated gasoline (required statewide April 1996) is expected to result in significant reductions of benzene and 1,3-butadiene emissions from engines burning reformulated gasoline.

E. INDOOR SOURCES OF 1,3-BUTADIENE

Environmental tobacco smoke (ETS) is the primary source of 1,3-butadiene in the indoor environment. Brunnemann et al. (1989) measured 1,3-butadiene concentrations of 205 to 361 μg/cigarette in sidestream smoke from seven different types of cigarettes. Concentrations of 1,3-butadiene in mainstream smoke ranged from 16 to 75 μg/cigarette. Lofroth et al. (1989) found 1,3-butadiene concentrations to average 400 μg/cigarette in a chamber where sidestream smoke had been directed from machine-smoked cigarettes. Another source of 1,3-butadiene indoors is vehicle exhaust which can infiltrate into homes near busy freeways or busy roadways. Information on exposure to 1,3-butadiene from indoor sources can be found in Chapter IV C and E.

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IV.
EXPOSURE TO 1,3-BUTADIENE

A. AMBIENT MONITORING FOR 1,3-BUTADIENE

The ARB's toxic monitoring network is comprised of 20 toxic monitoring stations (see Figure IV-1), nine of which are located in Southern California (south of Bakersfield), while the other 11 are located in the northern portion of the state. The monitoring sites and equipment locations were selected in accordance with the US EPA's site criteria document Probe Siting Criteria for Ambient Air Quality Monitoring, found in Appendix E of 40 CFR Chapter 1, Part 58. Data used in the exposure analysis were collected during the period of July 1988 through June 1989. The data for this period (hereafter referred to as "the study period") represent the most recent period for which the available data are known to be of consistent and verifiable quality. Individual 24-hour samples were collected and subsequently analyzed for 1,3-butadiene using gas chromatography with photoionization and a flame ionization detector. (For a complete description of the standard operating procedure for the determination of 1,3-butadiene in ambient air, please see Appendix B).

B. AMBIENT CONCENTRATIONS OF 1,3-BUTADIENE

The 1,3-butadiene data for the study period represents 20 sites and a percentage of all possible days during the sampling period. The months during which data are available for each site are summarized in Table IV-1.

1. Study Period Data Collected

The number of samples available per site during the study period range from 12 to 24 in Northern California, and 12 to 23 in Southern California. Sampling days were randomly selected; the Northern and Southern California sites averaged 1.6 observations per month.

Only 12 percent of the observations were below the limit of detection (LOD). In August 1988, the MLD staff changed the analysis technique for 1,3-butadiene resulting in a lowering of the LOD from 0.10 ppbv

Figure IV-1
The ARB's Toxic Monitoring Network for 1,3-Butadiene
(July 1988--June 1989)

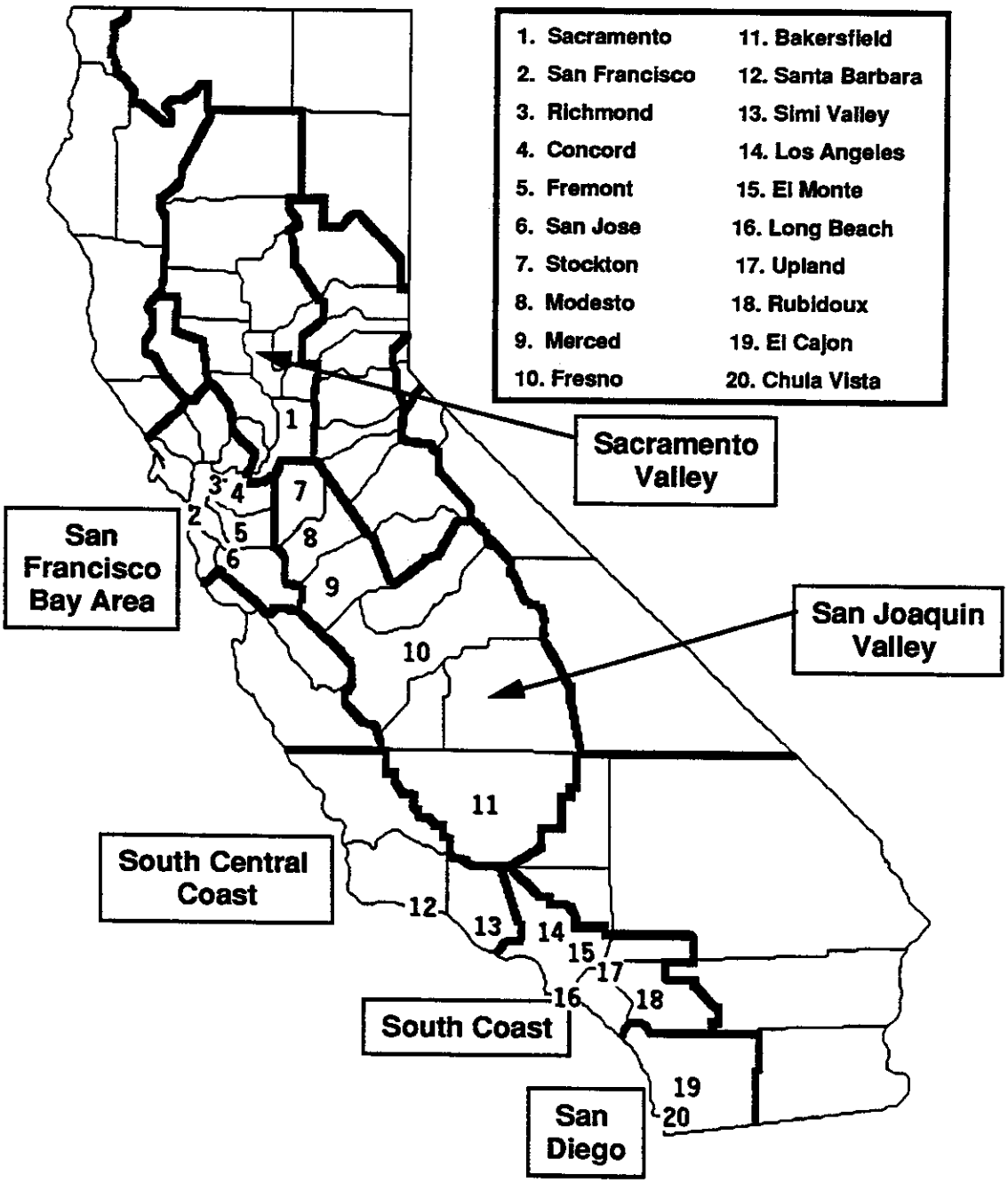


Table IV-1
Summary of 1,3-Butadiene Data*
July 1988 - June 1989

Air Basin / Site Location	J	A	S	O	N	D	J	F	M	A	M	J	Samples
South Coast Air Basin													
El Monte	o	o	o	o	o	o	o						12
Los Angeles	o				o	o	o	o	o	o	o	o	15
Long Beach	o	o	o	o	o	o	o	o	o		o	o	20
Rubidoux	o	o	o	o	o	o	o	o	o	o	o	o	20
Upland	o	o		o	o	o	o	o	o	o	o	o	21
South Central Coast Air Basin													
Santa Barbara	o			o	o	o	o	o	o	o	o	o	16
Simi Valley	o			o	o	o	o	o	o	o	o	o	23
San Diego Air Basin													
Chula Vista	o	o	o	o	o	o	o	o	o	o	o	o	22
El Cajon	o	o	o	o	o	o	o	o	o	o	o	o	20
San Francisco Bay Area Air Basin													
Concord	o			o	o	o	o	o	o	o	o	o	20
Fremont	o	o	o	o	o	o	o	o	o	o	o	o	22
Richmond	o	o	o	o	o	o	o		o	o	o	o	20
San Francisco	o				o	o	o	o	o	o	o	o	17
San Jose	o			o	o	o	o	o	o	o	o	o	20
San Joaquin Valley Air Basin													
Bakersfield	o	o	o	o	o	o	o	o	o	o	o	o	21
Fresno	o	o		o	o	o	o	o	o	o	o	o	20
Merced	o			o	o	o		o	o				12
Modesto	o	o	o	o	o	o	o	o	o	o	o	o	24
Stockton	o			o	o		o	o	o	o	o	o	16
Sacramento Valley Air Basin													
Citrus Heights	o			o	o	o	o	o	o	o	o	o	17

* An "o" indicates that at least one sample was collected during the month.

(0.22 $\mu g/m^3$) to 0.04 ppbv (0.09 $\mu g/m^3$). Observations below the LOD are referred to as partially observed data (POD). The number of POD samples for each site are included in Table IV-2.

Table IV-2

Estimated Mean[a] Annual 1,3-Butadiene Concentrations (in ppbv*) Using Four Methods for Estimating Values Below the LOD
July 1988 - June 1989

Air Basin / Site Location	POD=0 Mean	POD=0.02 Mean	POD=0.04 Mean	Gleit Mean	POD Samples
South Coast Air Basin					
El Monte	0.58	0.58	0.58	0.58	0
Los Angeles	0.47	0.47	0.47	0.47	0
Long Beach	0.38	0.38	0.38	0.38	1
Rubidoux	0.23	0.24	0.25	0.35	3
Upland	0.29	0.29	0.29	0.29	0
Basin Summary	0.41	0.42	0.42	0.42	4
South Central Coast Air Basin					
Santa Barbara	0.30	0.30	0.30	0.30	1
Simi Valley	0.13	0.13	0.14	0.14	5
Basin Summary	0.22	0.22	0.22	0.22	6
San Diego Air Basin					
Chula Vista	0.15	0.16	0.17	0.17	5
El Cajon	0.36	0.37	0.38	0.37	3
Basin Summary	0.26	0.27	0.28	0.27	8
San Francisco Bay Area Air Basin					
Concord	0.23	0.24	0.24	0.24	2
Fremont	0.19	0.20	0.20	0.20	3
Richmond	0.15	0.16	0.17	0.16	3
San Francisco	0.21	0.21	0.22	0.21	2
San Jose	0.42	0.42	0.42	0.42	1
Basin Summary	0.24	0.25	0.25	0.25	11
San Joaquin Valley Air Basin					
Bakersfield	0.28	0.28	0.28	0.28	2
Fresno	0.34	0.35	0.36	0.35	2
Merced	0.26	0.26	0.27	0.27	3
Modesto	0.27	0.28	0.29	0.28	4
Stockton	0.28	0.29	0.29	0.29	1
Basin Summary	0.29	0.29	0.30	0.29	12
Sacramento Valley Air Basin					
Citrus Heights	0.30	0.31	0.31	0.31	4

a. Means are computed as the sum of all observations divided by the total number of observations. This method is used in order to compare the effects of the different LOD values.

* 1 ppbv = 2.21 $\mu g/m^3$

POD were reported for each site (except for El Monte, Los Angeles, and Upland). Even though no value is reported when a concentration is below the LOD, important information is still available. The fewer POD there are, the less significant their impact on the analysis. Because removing these values from the dataset would bias the sample statistics and exposure estimates, four methods for dealing with POD were compared: (1) replacement of the values below the LOD with zero; (2) replacement of the values below the LOD with half the LOD; (3) replacement of the values below the LOD with the LOD; and (4) replacement of the values below the LOD with estimated order statistics (Gleit, 1985). The results of this comparison are presented in Table IV-2.

Since the 1,3-butadiene dataset has some data from the period when the LOD was 0.10 ppbv (0.22 $\mu g/m^3$) and some data when the LOD was 0.04 ppbv (0.09 $\mu g/m^3$), replacement values were calculated for each site and subset of data with a different LOD. Gleit's estimate was calculated for a subset with the higher LOD first, then the POD from the period of higher LOD were replaced by the estimated replacement value. Next, the same procedure was used to estimate a replacement value for any remaining POD. Both subsets of data for each site were then combined to form the overall dataset representing each site.

2. <u>Site-Specific Concentrations</u>

The range of concentrations sampled at each site during the study period are summarized in Table IV-3. Minimum, maximum, median and mean concentrations, as well as the standard deviation are reported for each site. Mean 1,3-butadiene concentrations were calculated as the mean of available monthly means to provide equal weighting for each month when the number of samples per month varies. Standard deviations were calculated from monthly means so they could be compared with the annual mean concentrations.

The site-specific ranges of the ambient 1,3-butadiene concentrations listed in Table IV-3 are plotted in Figure IV-2. Minimum concentrations range from POD at 17 of the 20 sites to 0.10 ppbv (0.22 $\mu g/m^3$) at El Monte, Los Angeles, and Upland. Maximum concentrations range in value from 0.34 ppbv (0.75 $\mu g/m^3$) at Richmond to 1.70 ppbv (3.75 $\mu g/m^3$) at San Jose.

Table IV-3
Summary of Ambient 1,3-Butadiene Data (in ppbv)
July 1988 - June 1989

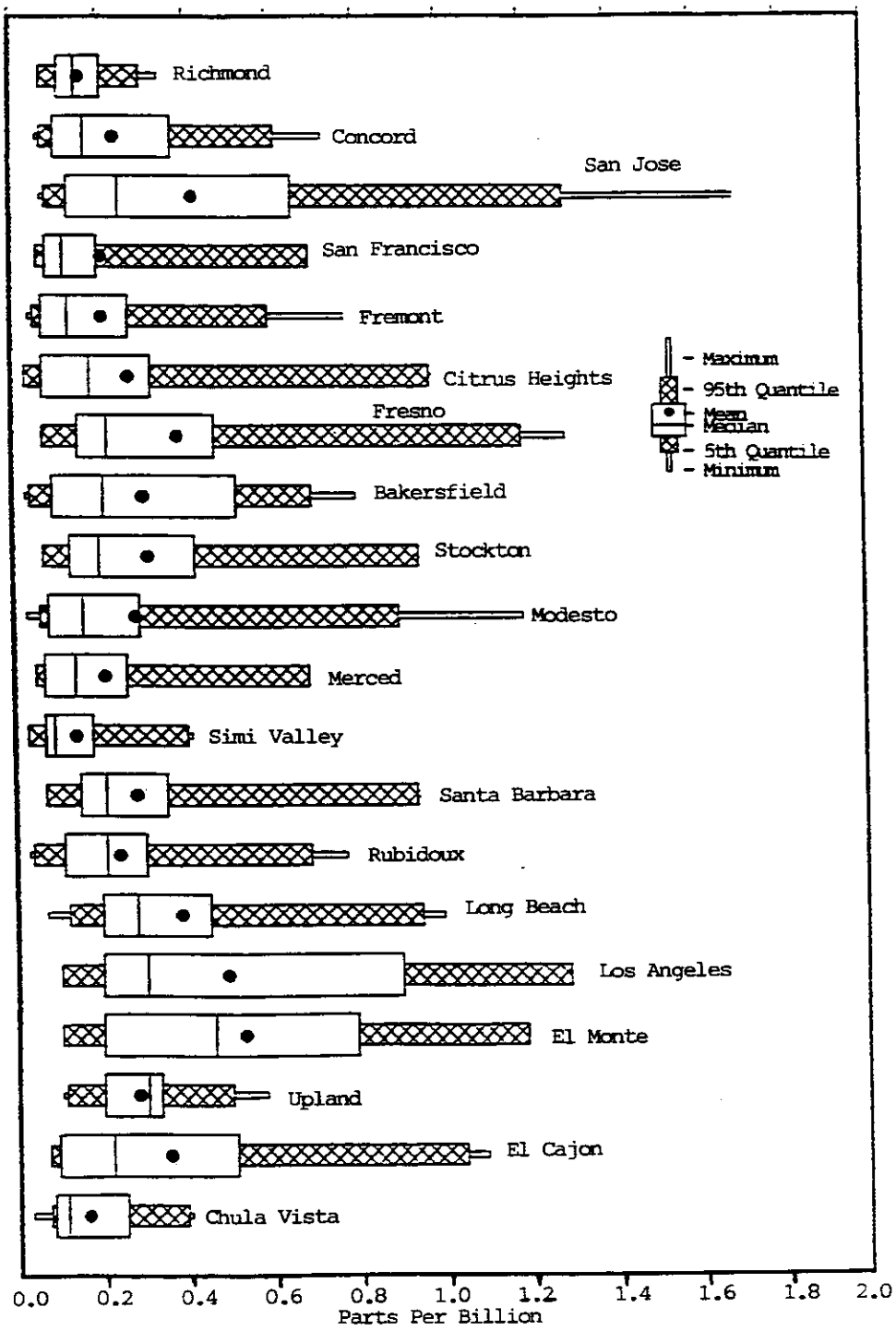
Air Basin Site Location	Minimum Conc.	Maximum Conc.	Median Conc.	Mean[a] Conc.	Standard[b] Deviation
South Coast Air Basin					
El Monte	0.10	1.20	0.46	0.58	0.37
Los Angeles	0.10	1.30	0.30	0.47	0.30
Long Beach	POD	1.00	0.28	0.38	0.26
Rubidoux	POD	0.77	0.21	0.25	0.19
Upland	0.10	0.58	0.30	0.29	0.12
Basin Summary	POD	1.30	0.31	0.39	0.26
South Central Coast Air Basin					
Santa Barbara	POD	0.94	0.21	0.30	0.16
Simi Valley	POD	0.41	0.09	0.14	0.11
Basin Summary	POD	0.94	0.20	0.22	0.14
San Diego Air Basin					
Chula Vista	POD	0.40	0.11	0.17	0.11
El Cajon	POD	1.10	0.22	0.37	0.35
Basin Summary	POD	1.10	0.21	0.27	0.26
San Francisco Bay Area Air Basin					
Concord	POD	0.73	0.17	0.24	0.13
Fremont	POD	0.78	0.13	0.20	0.18
Richmond	POD	0.34	0.15	0.16	0.08
San Francisco	POD	0.70	0.12	0.21	0.17
San Jose	POD	1.70	0.25	0.42	0.33
Basin Summary	POD	1.70	0.15	0.25	0.20
San Joaquin Valley Air Basin					
Bakersfield	POD	0.80	0.21	0.28	0.23
Fresno	POD	1.30	0.22	0.35	0.27
Merced	POD	0.69	0.14	0.27	0.22
Modesto	POD	1.20	0.16	0.28	0.27
Stockton	POD	0.95	0.20	0.29	0.20
Basin Summary	POD	1.30	0.20	0.29	0.26
Sacramento Valley Air Basin					
Citrus Heights	POD	0.98	0.18	0.31	0.32

a. Site means were calculated as the mean of available monthly means. Basin means are the mean of the site means.

b. Site standard deviations were calculated from the monthly means. Basin standard deviations are pooled values of the standard deviations across sites within a basin.

* 1 ppbv = 2.21 $\mu g/m^3$

Figure IV-2
Mean Annual 1,3-Butadiene Concentrations
Plotted Using Extended Box Plots
(July 1988--June 1989)



Mean annual concentrations ranged from a minimum of 0.14 ppbv (0.31 $\mu g/m^3$) at Simi Valley to a maximum of 0.58 ppbv (1.28 $\mu g/m^3$) at El Monte. Basin averages range from a minimum of 0.22 ppbv (0.48 $\mu g/m^3$) in the South Central Coast Air Basin to a maximum of 0.39 ppbv (0.86 $\mu g/m^3$) in the South Coast Air Basin.

3. Basin-Wide Mean Concentrations

The highest basin-wide mean concentration occurred in the South Coast Air Basin (0.42 ppbv = 0.93 $\mu g/m^3$), followed by the San Joaquin Valley Air Basin (0.29 ppbv = 0.64 $\mu g/m^3$), San Diego Air Basin (0.27 ppbv = 0.60 $\mu g/m^3$), San Francisco Bay Area Air Basin (0.25 ppbv = 0.55 $\mu g/m^3$), and South Central Coast Air Basin (0.22 ppbv = 0.48 $\mu g/m^3$).

4. Population-Weighted Exposure Estimates

Mean population-weighted exposure estimates were calculated using the study period 1,3-butadiene data. Exposures for the South Coast Air Basin and San Francisco Bay Area Air Basin were estimated by interpolating station values to census tract centroids. For the other air basins, a basin-wide mean concentration was estimated from the means for all sites in the basin. It was then assumed that all people in those counties with a sampling site were exposed to this estimated basin-wide mean concentration. Population data used in the exposure analysis represent 1980 census data updated to 1985 levels. The results of the exposure analysis are summarized in Table IV-4.

Included in Table IV-4 are Bootstrap confidence bounds (Efron, 1982), provided as a measure of uncertainty in the exposure estimates. The larger the difference between the mean annual exposure estimate and the upper and lower bounds, the greater the uncertainty in the estimate; the bounds are not provided as an upper or lower bound to actual exposure. The upper and lower bounds for each site were calculated by resampling the monthly means.

The mean population-weighted 1,3-butadiene exposure estimate for California is 0.37 ppbv (0.82 $\mu g/m^3$). A total of 20.3 million people are estimated to reside in the study areas. Basin-specific, population-weighted mean concentrations range from a minimum of 0.22 ppbv (0.48 $\mu g/m^3$) in the South Central Coast Air Basin to a maximum of 0.44 ppbv (0.97 $\mu g/m^3$) in the South Coast Air Basin.

Table IV-4
Summary of 1,3-Butadiene Population-Weighted Exposure Estimates
July 1988 - June 1989

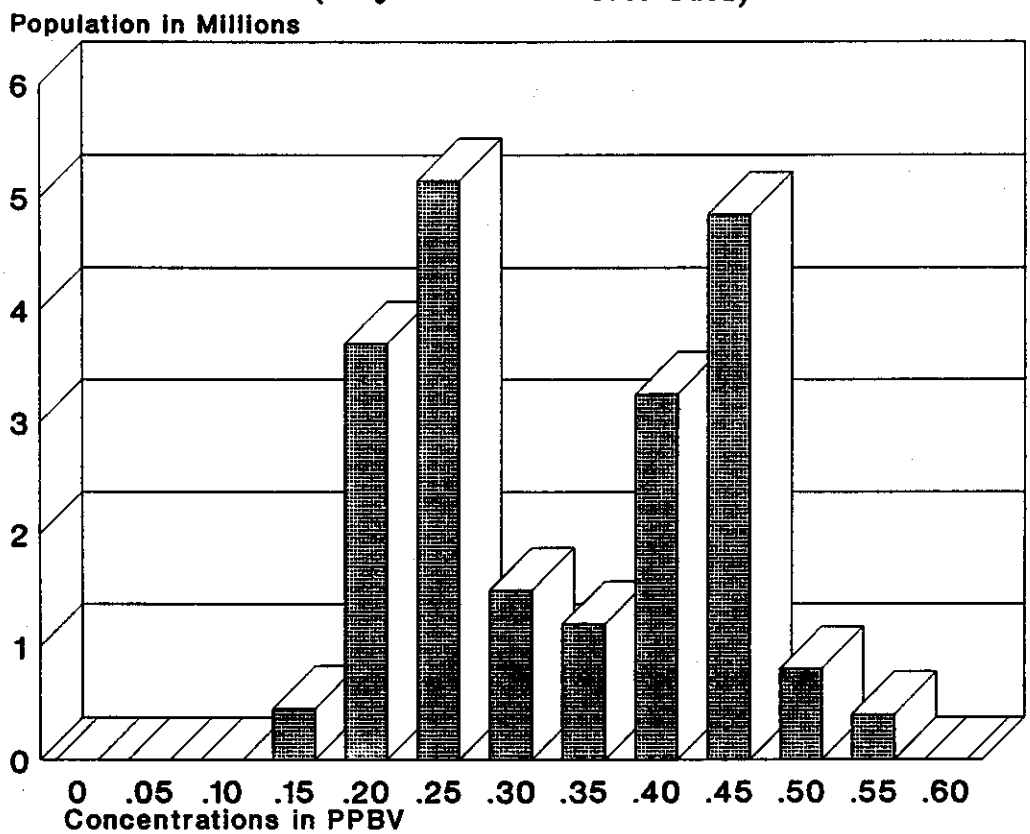
Air Basin Site Location	Upper Bound (ppbv)	Mean Exposure (ppbv)	Lower Bound (ppbv)	Population
South Coast Air Basin				
El Monte	0.80	0.58	0.34	
Los Angeles	0.62	0.47	0.30	
Long Beach	0.48	0.38	0.23	
Rubidoux	0.31	0.25	0.14	
Upland	0.37	0.29	0.22	
POPULATION-WEIGHTED EXPOSURE FOR SoCAB		**0.44**		10,092,133
South Central Coast Air Basin				
Santa Barbara	0.37	0.30	0.20	
Simi Valley	0.20	0.14	0.08	
POPULATION-WEIGHTED EXPOSURE FOR SCCAB		**0.22**		925,822
San Diego Air Basin				
Chula Vista	0.19	0.17	0.10	
El Cajon	0.55	0.37	0.20	
POPULATION-WEIGHTED EXPOSURE FOR SDAB		**0.27**		2,135,872
San Francisco Bay Area Air Basin				
Concord	0.27	0.24	0.15	
Fremont	0.27	0.20	0.12	
Richmond	0.18	0.16	0.11	
San Francisco	0.33	0.21	0.12	
San Jose	0.60	0.42	0.25	
POPULATION-WEIGHTED EXPOSURE FOR SFBAAB		**0.25**		4,394,374
San Joaquin Valley Air Basin				
Bakersfield	0.37	0.28	0.15	
Fresno	0.51	0.35	0.22	
Merced	0.44	0.27	0.14	
Modesto	0.39	0.28	0.14	
Stockton	0.35	0.29	0.16	
POPULATION-WEIGHTED EXPOSURE FOR SJVAB		**0.29**		1,901,243
Sacramento Valley Air Basin				
Citrus Heights	0.50	0.31	0.15	
POPULATION-WEIGHTED EXPOSURE FOR SVAB (Sac.County only)		**0.31**		889,806
OVERALL POPULATION-WEIGHTED EXPOSURE		**0.37**		20,339,250

* 1 ppbv = 2.21 $\mu g/m^3$

Figure IV-3 shows the total number of people exposed to various mean annual 1,3-butadiene concentrations (rounded off to the nearest 0.05 ppbv). The peak at 0.45 ppbv (1 $\mu g/m^3$) represents the population in the South Coast Air Basin, while the peak at 0.25 ppbv (0.55 $\mu g/m^3$) represents the remaining five air basins.

The overall geographic mean 1,3-butadiene concentration was 0.29 ppbv (0.64 $\mu g/m^3$). This value is approximately 22 percent lower than the population-weighted exposure estimate of 0.37 ppbv (0.82 $\mu g/m^3$), indicating that the highest concentrations of 1,3-butadiene tended to be in the areas of higher population density.

Figure IV-3
Estimated Mean Annual 1,3-Butadiene Exposure
(July 1988--June 1989 Data)



C. SOUTH COAST AIR QUALITY STUDY (SCAQS) 1,3-BUTADIENE CONCENTRATIONS DATA

The 1987 SCAQ Study (the first comprehensive study of air pollution in the South Coast Air Basin) provided a unique opportunity to characterize gaseous and

particulate pollutants in the basin under well-documented meteorological conditions. The sampling and analysis methods used in the study resulted in a data base that represents the 1,3-butadiene concentrations for a specific hour of a sampling day (as opposed to the data from the ARB's toxic monitoring network which represents 24-hour averages).

SCAQS air samples for the gaseous pollutants were drawn, over the period of 1 hour, into SUMMA polished stainless steel canisters. Analysis was performed using a gas chromatography/flame ionization detector. The data base represents the period of June 1987 through December 1987 (SCAQS, 1991). Average 1,3-butadiene concentrations from the eight monitoring sites in the SoCAB were 1.6 ppbv (3.53 $\mu g/m^3$), with minimum concentrations that ranged from below the limit of detection (LOD) of 0.1 ppbv (0.22 $\mu g/m^3$) to a high of 17.7 ppbv (39.1 $\mu g/m^3$). In comparison, data derived from the ARB's toxics monitoring network (July 1988 through July 1989 from samples drawn over 24 hours on random days) for the SoCAB show minimum, average, and maximum concentrations of below LOD, 0.39, and 1.3 ppbv, respectively (see Table IV-3).

D. INDOOR AIR CONCENTRATIONS OF 1,3-BUTADIENE

A limited number of studies have measured 1,3-butadiene concentrations indoors. Lofroth et al. (1989) investigated the chemical composition of environmental tobacco smoke (ETS) in a tavern where commercial cigarettes were smoked by occupants. The tavern was approximately 180 cubic meters in volume and was variously occupied by 5 to 25 individuals, many of whom were smoking. The 1,3-butadiene concentrations were from 2-hour sampling periods (both indoors and outdoors) on two separate study days. For the first study day, the 1,3-butadiene concentration was 8.60 ppbv (19 $\mu g/m^3$) indoors and less than the LOD (0.45 ppbv or 1 $\mu g/m^3$) outdoors. For the second study day, investigators measured 4.98 ppbv (11 $\mu g/m^3$) 1,3-butadiene indoors and 0.45 ppbv (1 $\mu g/m^3$) outdoors. Similar findings were obtained by the same investigators in a related chamber study using machine-smoked cigarettes.

Brunnemann et al. (1989) sampled air in a bar where an average of 5 to 15 cigarette smokers were present at any time. Continuous sampling over a 3-hour period yielded 1,3-butadiene concentrations ranging from 1.49 to 2.04 ppbv (3.3 to 4.5 $\mu g/m^3$).

A recent study sponsored by the ARB measured indoor levels of 1,3-butadiene in 62 Woodland California homes during the summer of 1990 (Sheldon, 1991). Air samples were collected in 6-liter SUMMA polished steel canisters. The sample was slowly drawn into the evacuated canister over 24 hours via a restrictive orifice attached to the canister valve. Interestingly, only 5 homes (8.1 percent of those sampled) had 1,3-butadiene concentrations above the LOD (0.54 ppbv or 1.2 $\mu g/m^3$). Results indicate that the concentrations in these homes ranged from 1.22 to 4.53 ppbv (2.7 to 10.0 $\mu g/m^3$). In 4 of the 5 homes with measurable 1,3-butadiene, 20 to 40 cigarettes reportedly were smoked during the monitoring period. The source of 1,3-butadiene in the other home with measurable 1,3-butadiene is uncertain.

An initial expectation is that homes in which many cigarettes were reportedly smoked would have measurable levels of 1,3-butadiene. However, smoking occurred in 16 of the 57 homes where indoor concentrations of 1,3-butadiene were less than the LOD. There are several possible reasons why 1,3-butadiene was not detected in more study homes with ETS. Since the study was designed to measure multiple air pollutants in the same sample, the LOD for 1,3-butadiene was relatively high (0.54 ppbv or 1.2 $\mu g/m^3$). Some of the homes may have had very high air exchange rates during the monitoring period; this can have a major effect on indoor pollution levels. Brunnemann et al. (1989) measured 1,3-butadiene in a 16 cubic meter laboratory (both with and without ventilation) while 5 to 10 cigarettes were being machine smoked. When the lab was unventilated, the 1,3-butadiene concentration was 4.30 ppbv (9.5 $\mu g/m^3$). When the lab was ventilated at 12 air exchanges per hour, the 1,3-butadiene level was 0.34 ppbv (0.75 $\mu g/m^3$). Another possible reason for the many measurements below the LOD in the Woodland study is that 1,3-butadiene is known to react with acrolein, another component of ETS (Harke et al., 1970, as reported by Brunnemann et al., 1989).

In the Woodland pilot study (November 1989), 3 of the 4 homes sampled had measurable levels of 1,3-butadiene (Sheldon et al., 1990). The measured indoor concentrations ranged from below the LOD of 0.05 ppbv (0.12 $\mu g/m^3$) up to 0.47 ppbv (1.04 $\mu g/m^3$). It is not known if ETS was present in these homes. The indoor concentrations were lower than the measured outdoor concentrations of 0.67 and 0.76 ppbv (1.48 and 1.67 $\mu g/m^3$).

E. ESTIMATES OF EXPOSURE FROM INDOOR AIR

Information on 1,3-butadiene concentrations in homes or public buildings is limited at this time. Indoor concentrations of 1,3-butadiene are primarily dependent upon the presence of ETS. On any given day, 43 percent of adult non-smokers report that they are near ETS. The proportion of non-smoking youths (age 12 through 17) exposed to an ETS environment on any given day is even higher at 64 percent (Jenkins et al., 1992). Therefore, indoor air is almost certainly the major route of exposure to 1,3-butadiene for individuals who are exposed to an ETS environment.

Exposure estimates for short-term exposure in a bar or tavern are presented in Table IV-5. Concentrations of 1,3-butadiene measured by Lofroth et al. (1989) and Brunnemann et al. (1989) are the basis for the short duration calculation. The exposure duration used is 3 hours, the average time spent in a bar or nightclub (Jenkins et al., 1992). The assumed breathing volume is 1.06 cubic meters per hour (based on an average breathing volume of 20 cubic meters of air per day). An average of 3 cubic meters of air are breathed during 8 hours of sleep, while an average 1.06 cubic meters per hour are breathed during the remaining 16 hours of the day (International Commission on Radiological Protection, 1975). Based on measurements of 1,3-butadiene in a tavern, bar, and an unventilated lab, the estimated dose of 1,3-butadiene inhaled in 3 hours in an ETS environment could range from 10 to 60 μg. The exposure estimate for a well-ventilated indoor environment (ventilated lab) with ETS is much lower at 2.4 μg of 1,3-butadiene during 3 hours. The exposure estimate for an individual inhaling the statewide outdoor average concentration of 1,3-butadiene for 3 hours is 2.6 μg.

Restaurants also provide opportunities for exposure to an ETS environment. Restaurants are visited by 35 percent of the California population for an average duration of 81 minutes on any given day (Jenkins et al., 1992). Elevated indoor 1,3-butadiene concentrations in such places can lead to a large increase in total exposure for the individual who spends time in these microenvironments. The actual amount of 1,3-butadiene inhaled from ETS exposure will vary due to room size, room ventilation rates, the number of cigarettes smoked, and other factors.

Residential concentrations data for 1,3-butadiene are too limited at this time to generate exposure estimates. However, it is apparent that the potential for indoor exposure can exceed outdoor exposure. Further measurements are needed in a wide variety of homes and offices and over different seasons in order to quantify typical indoor butadiene exposures. Such measurements may also help to further identify the relationships between smoking and indoor levels, and between indoor and outdoor levels of 1,3-butadiene.

Table IV-5
3 Hour Estimated Inhaled Doses of 1,3-Butadiene in Environments with ETS

LOCATION	REFERENCE	INDOOR CONCENTRATION (ppbv)	INDOOR CONCENTRATION (μg/cubic meter)	ESTIMATED INHALED[d] DOSE (μg/exposure)
Tavern	1	5.0-8.6[a]	11-19	35-60
Bar	2	1.5-2.0[a]	3.3-4.5	10-14
Unventilated Lab	2	4.3[b]	9.5	30
Ventilated Lab	2	0.3[c]	0.75	2.4

References: 1) Lofroth et al., 1989. 2) Brunnemann et al., 1989.

a: Range of 2 samples. b: Mean of 4 experimental runs. c: Mean of 2 samples.
d: Estimated dose =
indoor concentration x air breathed/hour x # of hours at that location
(μg/cubic meter) (1.06 cubic meters/hr) (3 hours)

F. NEAR-SOURCE ("HOT SPOT") EXPOSURE

Some Californians may be exposed to near-source, or "hot spot" concentrations of 1,3-butadiene added to the average ambient concentration of 1,3-butadiene. "Hot spot" exposure to airborne 1,3-butadiene may significantly increase the cancer risk to individuals living near sources. Sources of "hot spot" emissions of 1,3-butadiene may include facilities using butadiene for production of resins and polymers, synthetic rubber manufacturing facilities, chemical production facilities, petroleum refineries, and stationary fuel combustion sources.

The US EPA has roughly estimated that 1,3-butadiene exposure for individuals living near two facilities in California may be almost double the average exposure experienced by individuals not living near these facilities (see Part B's Section 5.2 on Hot Spots). However, the ARB staff does not have enough emissions and exposure information available at this time to validate the US EPA's estimate. This information is expected during 1992, when the ARB staff will evaluate 1,3-butadiene emissions data reported by facilities under the AB 2588 Air Toxics "Hot Spots" emissions reporting program. If the Board identifies 1,3-butadiene as a toxic air contaminant, this "hot spot" information will be used during the risk management phase to help determine priority and need for control of sources emitting 1,3-butadiene.

G. OTHER ROUTES OF 1,3-BUTADIENE EXPOSURE

1. Water Ingestion

Detectable concentrations of 1,3-butadiene have been reported in drinking water by the International Agency for Research on Cancer (IARC, 1986). The investigators referenced by IARC did not say how much 1,3-butadiene had been detected, only that it had been.

1,3-Butadiene has been listed as a carcinogen under the California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65; Health and Safety Code Section 25249.5). Substances listed under Proposition 65 have not necessarily been measured in water, but are listed due to their toxicity and their potential release into water. According to the California Department of Health Services (DHS), 1,3-butadiene has not been found in California's ground water. Polybutylene pipe (used in water systems) was investigated by the DHS as a possible source of 1,3-butadiene contaminating water supplies (Spath, 1989). It was not found in tests of water from these types of pipes (Cooper, 1989).

2. Food

There is limited information regarding the level of 1,3-butadiene in food. Butadiene is used to make food packaging, vegetable oil bottles, chewing gum bases, and lids for certain containers such as those for yogurt and cottage cheese. McNeal and Breder (1987) investigated the migration of 1,3-butadiene from food containers to the food. They reported that for the five different types of containers tested, 1,3-butadiene was detected in the contents of only one of the containers (olive oil, which contained about 8 to 9 nanograms of 1,3-butadiene per gram of oil). No butadiene was detected in chewing gum bases.

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V.

ATMOSPHERIC FATE AND PERSISTENCE OF 1,3-BUTADIENE

A. PERSISTENCE OF 1,3-BUTADIENE

The atmospheric persistence and fates of chemical compounds emitted into the troposphere are governed by a number of chemical and physical removal processes (Finlayson-Pitts and Pitts, 1986). For the great majority of organic compounds (including 1,3-butadiene) the most important removal processes are photolysis, reaction with hydroxyl (OH) and nitrate (NO_3) radicals, and reaction with ozone (O_3).

1. Chemical Removal Mechanisms

The atmospheric lifetime (τ) of a chemical is defined as the time to decay to a concentration of 1/e (=0.368) of that initially present. Also,

$$\frac{1}{\tau} = \frac{1}{\tau_{chemical}} + \frac{1}{\tau_{physical}}$$

where $\tau_{chemical}$ and $\tau_{physical}$ are the lifetimes of the chemical with respect to only chemical reaction and only physical loss processes, respectively. These chemical and physical lifetimes are composites of those for the individual loss processes, for example:

$$\frac{1}{\tau_{chemical}} = \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{OH}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} \ldots$$

where $\tau_{photolysis}$, τ_{OH}, τ_{NO_3} and τ_{O_3} are the lifetimes with respect to photolysis, reaction with the OH radical, reaction with the NO_3 radical, and reaction with O_3, respectively.

The reactive loss processes are determined by the rate constants, k_x, for reaction and the ambient atmospheric concentrations, [X], of the reactive intermediates. For example:

$$\frac{1}{\tau_{OH}} = k_{OH}[OH]$$

For photolysis, the photolysis rate depends on the absorption cross section (σ), the photolysis quantum yield (ϕ), and the radiation intensity (J), all of which are wavelength dependent:

$$\frac{1}{\tau_{photolysis}} = k_{photolysis} = \int_{\sim 290\ nm}^{\sim 800\ nm} \sigma_\lambda\ \phi_\lambda J_\lambda d_\lambda$$

a. Reaction with OH Radicals

The available kinetic data of Lloyd et al. (1976), Atkinson et al. (1977), Barnes et al. (1982), Ohta (1983), Atkinson and Aschmann (1984) and Liu et al. (1988) are given in Table V-1 and are plotted in Arrhenius form in Figure V-1 (both adapted from Atkinson, 1989). The room temperature rate constants from Lloyd et al. (1976), Atkinson et al. (1977), Barnes et al. (1982), Ohta (1983), Atkinson and Aschmann (1984) and Liu et al. (1988) are in very good agreement. Furthermore, the temperature dependencies obtained by Atkinson et al. (1977) and Liu et al. (1988) are in good agreement.

A unit-weighted least-squares analysis of the absolute rate constant data of Atkinson et al. (1977) and Liu et al. (1988) at temperatures less than 500 K yields the Arrhenius expression of:

$$k(1,3\text{-butadiene};\ T < 500\ K) = (1.44^{+0.54}_{-0.40}) \times 10^{-11}\ e^{(448 \pm 117)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

over the temperature 299-483 K, where the indicated errors are two least-squares standard deviations.

The relative rate data of Atkinson and Aschmann (1984) for a series of alkenes and dialkenes, when combined with the literature absolute rate constants (Atkinson, 1989), leads to the recommendation of:

$$k(1,3\text{-butadiene}) = 6.78 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1} \quad \text{at 295 K.}$$

Combined with the above temperature dependence, this yields the recommended Arrhenius expression of:

$$k(1,3\text{-butadiene};\ T < 500\ K) = (1.48^{+0.56}_{-0.42}) \times 10^{-11}\ e^{(448 \pm 117)/T}\ cm^3\ molecule^{-1}\ s^{-1}$$

TABLE V-1

Rate Constants k and Arrhenius Parameters ($k = Ae^{-B/T}$) for the Gas-Phase Reactions of the OH Radical with 1,3-Butadiene

$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	B (K)	$10^{12} \times k$ (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
		67.6 ± 13.6	305 ± 2	RR [relative to k(n-butane) = 2.62×10^{-12}][a]	Lloyd et al. (1976)	
14.5	-468 ± 151	68.5 ± 6.9 57.2 ± 5.7 43.3 ± 4.4	299.5 347.2 424.0	FP-RF	Atkinson et al. (1977)	299-424
		65.0	300	RR [relative to k(ethene) = 8.44×10^{-12}][a]	Barnes et al. (1982)	
		61.6 ± 1.5	297 ± 2	RR [relative to k(propene) = 2.65×10^{-11}][a]	Ohta (1983)	
		68.8 ± 2.2	297 ± 2	RR [relative to k(2-methyl-2-butene) = 8.72×10^{-11}][a]	Ohta (1983)	
		67.8 ± 2.2	295 ± 1	RR [relative to k(propene) = 2.68×10^{-11}][a]	Atkinson and Aschmann (1984)	

(continued)

TABLE V-1 (cont.)

10^{12} x A (cm^3 molecule^{-1} s^{-1})	B (K)	10^{12} x k (cm^3 molecule^{-1} s^{-1})	at T (K)	Technique	Reference	Temperature range covered (K)
		61 ± 6	313	PR-RA	Lin et al. (1988)	313-1203
		50 ± 5	333			
		51 ± 5	338			
		46 ± 5	373			
		41 ± 4	393			
		47 ± 5	408			
		42 ± 4	438			
		35 ± 4	483			
		29 ± 3	563			
14 ± 1	-440 ± 40 (313-623 K)	30 ± 3	623			
		30 ± 3	673			
		24 ± 3	723			
		20 ± 2	773			
		17 ± 2	873			
		15 ± 2	923			
		11 ± 1	1023			
		10 ± 1	1053			
		6.5 ± 0.6	1153			
		6.9 ± 0.7	1173			
		7.7 ± 0.8	1203			

[a]Rate constant recommendations taken from Atkinson (1988).

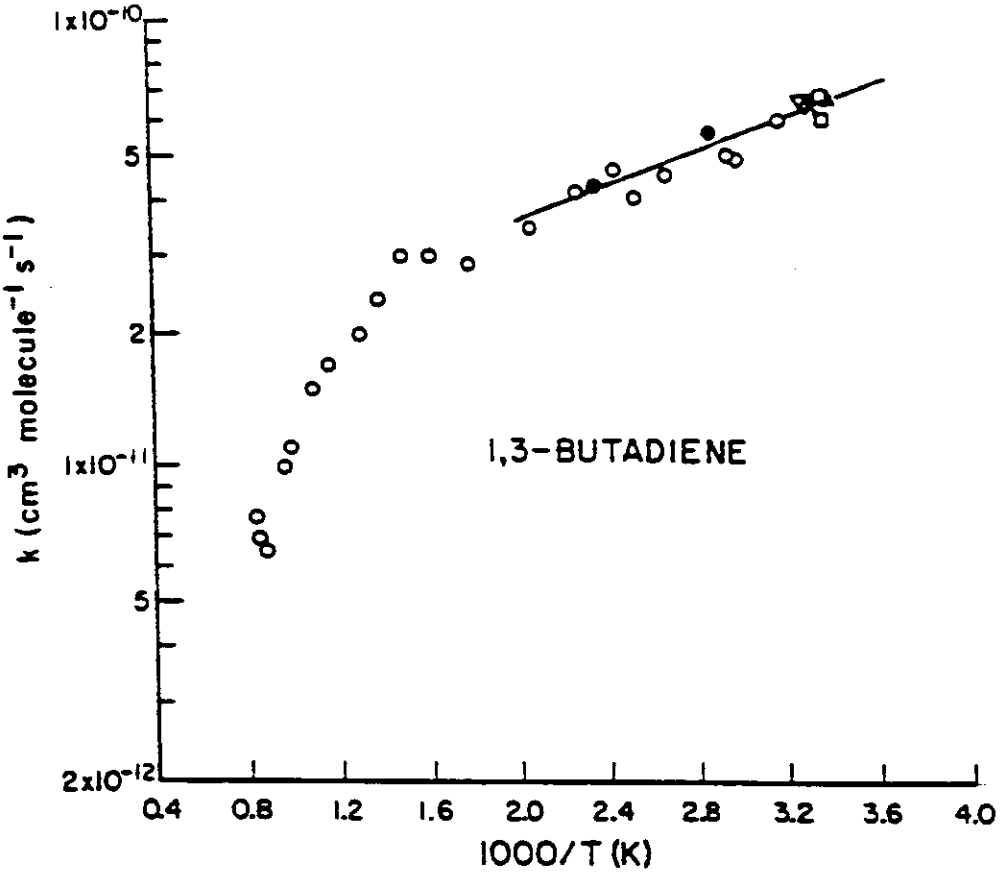


Figure V-1 Arrhenius plot of rate constants for the reaction of the OH radical with 1,3-butadiene. (▽) Lloyd et al. (1976); (●) Atkinson et al. (1977); (x) Barnes et al. (1982); (□) Ohta (1983); (△) Atkinson and Aschmann (1984); (○) Liu et al. (1988); (———) recommendation (see text).

over the temperature range 295-483 K, where the indicated errors are two least-squares standard deviations, and

$$k(1,3\text{-butadiene}) = 6.66 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K},$$

with an estimated overall uncertainty at 298 K of ± 20 percent. Using the Arrhenius expression given above, the OH rate constant at 265 K is

$$8.03 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

The relative rate constants of Lloyd et al. (1976), Barnes et al. (1982) and Ohta (1983) are in very good agreement with this recommendation. By analogy with the alkenes such as ethene, propene and the butenes, this rate

constant (for the OH radical addition pathway) will be very close to the high-pressure limit, at least up to around 500 K. The recommendation (Atkinson, 1989) provides a good fit to the rate constants measured by Liu et at. (1988) in one atmosphere of argon diluent up to around 700 K.

Using the rate constants cited above for the gas-phase reactions of OH radicals with 1,3-butadiene combined with an estimated ambient atmospheric concentration of 1.5×10^6 molecule/cm^3 during a 12-hour daytime period (Prinn et al., 1987), the calculated atmospheric lifetime of 1,3-butadiene with respect to reaction with OH radicals ranges from 2.3 to 2.8 hours.

b. Reaction with Nitrate Radicals

Kinetics data for the reaction of NO_3 radicals with 1,3-butadiene have been obtained by Canosa-Mas et al. (1988), Rahman et al. (1988) and Atkinson et al. (1988). These data are summarized in Table V-2. The recommended rate constant of:

$$k(1,3\text{-butadiene}) = (1.0 \pm 0.2) \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1} \text{ at } 298\ K$$

for the reaction of NO_3 radicals with 1,3-butadiene is based upon the study of Atkinson et al. (1988).

Table V-2
Room Temperature Rate Constants for the Gas-Phase Reaction of the NO_3 Radical with 1,3-Butadiene

$k(cm^3\ molecule^{-1}\ s^{-1})$	Reference
$(2.2 \pm 0.6) \times 10^{-13}$	Canosa-Mas et al. (1988)
$(1.7 \pm 0.3) \times 10^{-13}$	Rahman et al. (1988)
$(9.79 \pm 1.17) \times 10^{-14}$	Atkinson et al. (1988)

Using a tropospheric concentration for NO_3 radicals during a 12-hour nighttime period of 2.4×10^8 molecule/cm^3 (Platt et al. 1984; Atkinson et al. 1986) and the reaction rate constant for NO_3 radicals listed above, the atmospheric lifetime of 1,3-butadiene with respect to gas-phase reactions with NO_3 radicals ranges from 9 to 13 hours.

c. Reaction with Ozone

Kinetic data for the gas-phase reaction of ozone with 1,3-butadiene have been obtained by Hanst et al. (1958), Japar et al. (1974), Becker et al. (1974), Toby and Toby (1975) and Bahta et al. (1984), and given in Table V-3.

Table V-3

Reported Rate Constants k and Arrhenius Parameters, $k = Ae^{-B/T}$, for the Reaction of O_3 with 1,3-Butadiene

A (cm^3 $molecule^{-1}$ s^{-1})	B (K)	$10^{18} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	At T (K)	Technique	Reference	Temperature Range Covered (K)
		8.1	a	F/S-IR	Hanst et al. (1958)	
		8.4 ± 0.2	299 ± 2	S-CL	Japar et al. (1974)	
5.45×10^{-14}	2682 ± 101	6.7[b]	298	S-UV	Becker et al. (1974)	~286-358[b]
1.05×10^{-13}	2919 ± 403	7.5 ± 1.3[d]	303	S-UV	Toby and Toby (1975)	273-343
2.20×10^{-14}	2430 ± 55	6.3[b]	298	S-UV	Bahta et al. (1984)	254-299

[a]Room temperature.

[b]Calculated from the Arrhenius expression.

[c]Derived from graphical tabulations given.

[d]Value cited by Toby et al. (1976).

The data from all these studies are in reasonable agreement. Since the individual rate constants at the temperatures studied were not given by Becker et al. (1974) or Toby and Toby (1975), a least-squares analysis of the entire data set cannot be carried out.

A unit-weighted average of the room temperature rate constants of Hanst et al. (1958), Japar et al. (1974), Becker et al. (1974) and Bahta et al. (1984) [neglecting the rate constant study of Toby and Toby (1975) because of the magnitude of the error limits associated with it] leads to:

$$k(O_3 + \text{1,3-butadiene}) = 7.4 \times 10^{-18}\ cm^3\ molecule^{-1} s^{-1} \text{ at } 298\ K.$$

Combining this 298 K rate constant with a temperature dependence of B=2500 K derived from the temperature dependencies of Becker et al. (1974) and Bahta et al. (1984) leads to the recommendation of:

$$k(O_3 + \text{1,3-butadiene}) = 3.26 \times 10^{-14}\ e^{-2500/T}\ cm^3\ molecule^{-1}\ s^{-1}.$$

At 265 K (the average temperature of the troposphere), the rate constant is $2.6 \times 10^{-18}\ cm^3\ molecule^{-1}\ s^{-1}$.

Using a tropospheric concentration for O_3 during a complete 24-hour day of 7×10^{11} molecule/cm^3 (Logan, 1985) and the rate constants listed above, the calculated atmospheric lifetime of 1,3-butadiene due to reaction with O_3 ranges from 2.2 to 6.4 days.

d. Reactions with Other Chemical Species

None of the other reactive species in the troposphere are expected to react with 1,3-butadiene, at least not at rates which are significant relative to its rate of reaction with OH and NO_3 radicals or with O_3.

e. Photolysis

1,3-Butadiene will not undergo photolysis in the actinic region (Calvert and Pitts, 1966).

2. Physical Removal Mechanisms

No data concerning the physical removal processes for 1,3-butadiene are

available. However, neither wet nor dry deposition is expected to be important as a loss process compared with the chemical reactions with OH and NO_3 radicals and O_3.

3. Atmospheric Formation Processes

No atmospheric formation processes for 1,3-butadiene have been identified.

B. FATE OF 1,3-BUTADIENE

1. OH Radical Reaction

Under atmospheric conditions, the reaction of the OH radical with 1,3-butadiene proceeds essentially entirely (greater than 99 percent) by initial OH radical addition (Atkinson, 1988):

$$OH + CH_2{=}CHCH{=}CH_2 \longrightarrow HOCH_2\dot{C}HCH{=}CH_2 \text{ and } \dot{C}H_2\dot{C}HOHCH{=}CH_2$$

These initially formed radicals will rapidly (usually faster than 1 microsecond) add O_2 to yield the peroxy radicals

$$HOCH_2\underset{\underset{OO^{\bullet}}{|}}{C}HCH{=}CH_2 \text{ and } \dot{O}OCH_2CHOHCH{=}CH_2$$

In the presence of NO, these peroxy radicals are expected to yield NO_2 and the corresponding alkoxy radical,

$$HOCH_2\underset{\underset{OO^{\bullet}}{|}}{C}HCH{=}CH_2 + NO \longrightarrow HOCH_2\underset{\underset{O^{\bullet}}{|}}{C}HCH{=}CH_2 + NO_2$$

$$\dot{O}OCH_2CHOHCH{=}CH_2 + NO \longrightarrow \dot{O}CH_2CHOHCH{=}CH_2 + NO_2$$

although it is possible that a small amount (less-than/about 5 percent) of an organic nitrate may be formed. For example:

$$HOCH_2\underset{\underset{OO^{\bullet}}{|}}{C}HCH{=}CH_2 + NO \longrightarrow HOCH_2\underset{\underset{ONO_2}{|}}{C}HCH{=}CH_2$$

When the NO mixing ratios are less-than/about 30 parts per trillion, the above peroxy radicals will react with HO_2 to form ROOH (hydroperoxides) and/or other

peroxy radicals (to form, at least in part, the above alkoxy radicals) in competition with the reactions with NO given above.

The alkoxy radicals shown above are expected to decompose rapidly.

$$HOCH_2\overset{O^{\bullet}}{C}HCH=CH_2 \longrightarrow CH_2OH + CH_2=CHCHO$$

$$\downarrow O_2$$

$$HCHO + HO_2$$

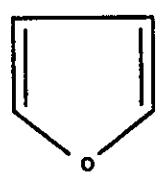
$$OCH_2CHOHCH=CH_2 \longrightarrow HCHO + CH_2=\overset{\bullet}{C}HCHOH$$

$$\downarrow O_2$$

$$CH_2=CHCHO + HO_2$$

Thus, in the presence of NO the major products are expected to be HCHO and CH_2=CHCHO, and this is observed.

Heuss and Glasson (1968) obtained approximately 30-40 percent yields of HCHO and CH_2=CHCHO (uncorrected for losses) in an irradiated NO-1,3-butadiene-air mixture. However, furan



has been observed as a minor product (approximately 4-6 percent) from the OH radical reaction with 1,3-butadiene, both in the presence and absence of NO (Ohta 1984, Atkinson et al. 1989).

2. <u>Nitrate Radical Reaction</u>

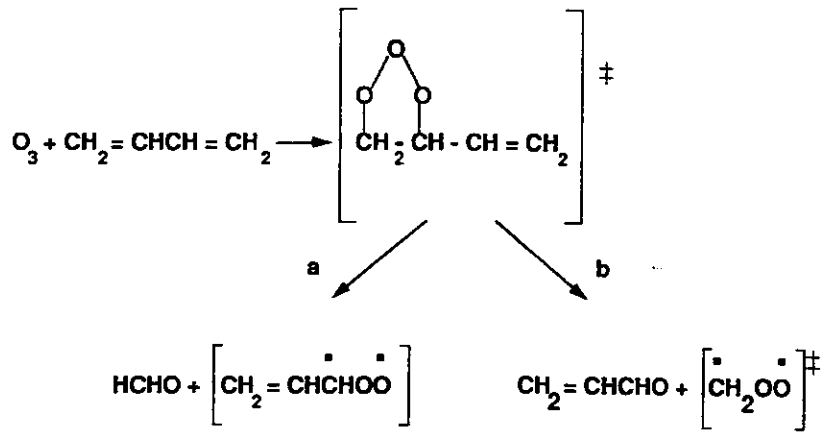
As for the OH radical reaction, the NO_3 radical reaction proceeds by initial addition

$$NO_3 + CH_2=CHCH=CH_2 \longrightarrow O_2NOCH_2\overset{\bullet}{C}HCH=CH_2 \text{ and } \overset{\bullet}{C}H_2\overset{ONO_2}{C}HCH=CH_2$$

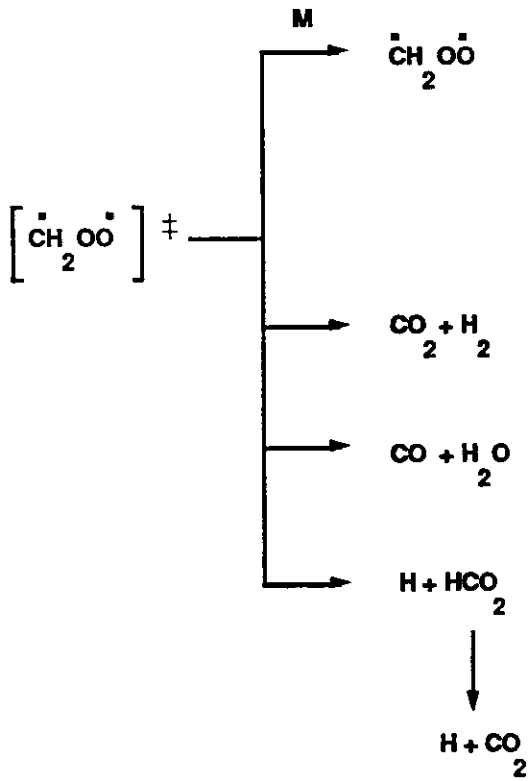
which will rapidly add O_2, and the resulting peroxy radicals are then expected to react to HO_2 radicals and/or other peroxy radicals. The reaction mechanisms and products formed from these reactions are as yet unknown.

3. Reaction with Ozone

As discussed by Atkinson and Carter (1984), the gas-phase reaction of O_3 with 1,3-butadiene involves initial addition to form an energy-rich "molozonide",



which is then expected to decompose rapidly, with the relative importance of pathways (a) and (b) not being known. The initially energy-rich $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical can be collisionally thermalized or decomposed (Atkinson and Carter, 1984):



with the thermalized biradical $\dot{C}H_2\dot{O}O$ reacting predominantly with water vapor under atmospheric conditions:

$$\dot{C}H_2\dot{O}O + H_2O \longrightarrow HCOOH + H_2O \text{ (formic acid).}$$

The fate of the $\left[CH_2{=}C\dot{H}C\dot{H}OO\right]^{\ddagger}$ biradical is not presently known.

The available data suggest that the major products of the O_3 reaction with 1,3-butadiene will be formaldehyde (HCHO) and acrolein ($CH_2 = CHCHO$), together with products including formic acid (HCOOH), CO, CO_2, H_2, and HO_2 radicals, which arise from subsequent reactions of the "Criegee" biradicals.

1,3-Butadiene will be removed from the atmosphere both by gas-phase reaction with OH radicals during the day and with NO_3 radicals at night, with calculated atmospheric lifetimes of a few hours and half a day, respectively, for the two processes. It has a half-life of approximately 1.6 to 9 hours in the atmosphere. Thus, 1,3-butadiene will be confined to a local radius of impact largely within the airshed in which it is emitted.

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Appendix A

Methods for Estimating Usage and Emissions of 1,3-Butadiene in California

Appendix A

Methods for Estimating Usage and Emissions
of 1,3-Butadiene in California

A. ON-ROAD MOTOR VEHICLES

The following table summarizes the 1,3-butadiene emissions for individual classes of on-road motor vehicles for inventory year 1990. The estimates are based on the total organic gas (TOG) from on-road vehicular exhaust and the 1,3-butadiene emission factors developed by the ARB's Mobile Source Division (MSD). The emission factors include an adjustment for the chemical stability of 1,3-butadiene in the exhaust (ARB, 1991a). Approximately 2,600 tons per year of 1,3-butadiene are emitted by this source category.

Summary of 1,3-Butadiene Emissions from On-road Vehicular Exhaust for Inventory Year 1990

	Daily Vehicle Miles Traveled[a]	TOG[a]	1,3-Butadiene	
	(1,000 miles)	(tons/day)	TOG Wt %[b]	tons/year
Light Duty Passenger				
Non-Catalyst	26,127	165.23	0.97	585
Catalyst	425,545	387.67	0.59	835
Diesel	11,799	4.21	0.90	14
Light Duty Truck				
Non-Catalyst	6,745	40.88	0.97	145
Catalyst	114,681	131.88	0.59	284
Diesel	3,254	1.2	0.90	4
Medium Duty Truck				
Non-Catalyst	3,369	22.65	0.97	80
Catalyst	32,782	43.22	0.59	93
Diesel	--	--	0.90	--
Heavy Duty Truck				
Non-Catalyst	12,717	38.22	0.97	135
Catalyst	7,708	5.32	0.59	11
Diesel	26,788	77.21	1.36	383
Buses	794	3.17	1.36	16
Motorcycles	4,107	13.34	0.97	47
Total		934.20		2,632

(continued on next page)

Table Notes:

a. ARB, 1990. Data retrieved from EMFAC7E/BURDEN7C for inventory year 1990 (1987 baseline). Emission Inventory Branch, Technical Support Division, Sacramento, CA.

b. ARB, 1991a. Internal ARB memorandum from K. D. Drachand to Terry McGuire regarding butadiene emission factors, dated July 17, 1991. Mobile Source Division, El Monte, CA.

"For the light-duty passenger (LDP) non-catalyst class, emission factors were developed using test data from 16 pre-1974 non-catalyst vehicles. For the LDP catalyst class, a total of 62 vehicles were tested including 55 three-way catalyst and 7 oxidation catalyst vehicles. For the LDP diesel class, two LDP diesel vehicles were tested. Only one heavy-duty (HD) diesel prototype vehicle was tested. The emission factor developed from this HD diesel vehicle was used for both the HD diesel trucks and urban bus classes.

The emission factor for the LDP non-catalyst vehicle class is assumed to be applicable to non-catalyst light-duty (LD), medium-duty (MD), HD gasoline trucks, and motorcycles. Similarly, the emission factor for the LDP catalyst vehicle class is assumed to be applicable to catalyst-equipped LD, MD, and HD gasoline trucks. The emission factor for the LDP diesel vehicle class is assumed to be applicable to LD and MD diesel trucks."

B. OTHER MOBILE SOURCES

Other mobile sources include off-road vehicles, boats, trains, ships, aircraft, mobile equipment and utility equipment. Emissions of 1,3-butadiene from this category are based on total organic gas (TOG) emissions for each of three types of combustion fuels (ARB, 1991b), speciation profile (distillate oil), and emission rates (diesel and gasoline) of 1,3-butadiene. The emissions are separately estimated and then added together for the statewide estimate. The staff estimates statewide emissions from this category to be approximately 1,100 tons of 1,3-butadiene per year.

1. Distillate Oil Combustion

The Air Resources Board's Speciation Manual (ARB, 1989b), contains species profiles by processes. The Speciation Manual lists 1,3-butadiene as a compound contained in Profile #9: Industrial Internal Combustion Engine-Distillate Oil. The weight fraction of 1,3-butadiene is listed as .0590 in this profile. Because there are no profiles for distillate oil combustion from other mobile sources available, the staff applied profile #9 to other mobile sources.

There are an estimated 779.36 tons per year of total organic gas (TOG) emissions statewide from distillate oil combustion of other mobile sources (ARB, 1989a). Emissions from residual oil combustion are also included in this statewide estimate. The staff estimated 1,3-butadiene emissions statewide from distillate oil combustion of other mobile sources as follows:

$$EMS_{Dis} = TOG_{Dis} \times W_{Dis}$$

Where:

EMS_{Dis}: Statewide 1,3-butadiene emissions from distillate oil combustion of other mobile sources (tons per year).

TOG_{Dis}: Statewide emissions of Total Organic Gas from distillate oil combustion of other mobile sources (tons per year).

W_{Dis}: Weight fraction of 1,3-butadiene to Total Organic Gas from distillate oil combustion of other mobile sources.

Substituting the values of TOG_{Dis} and W_{Dis}, the equation becomes:

$$EMS_{Dis} = \frac{779.36 \text{ Tons TOG}}{\text{Year}} \times \frac{.0590 \text{ Tons of 1,3-butadiene}}{\text{Ton of TOG}}$$

$$EMS_{Dis} = \frac{45.98 \text{ Tons of 1,3-butadiene}}{\text{Year}}$$

2. <u>Gasoline Combustion</u>

There is an estimated 83,580 tons per year of total organic gas (TOG) emissions statewide from gasoline combustion of other mobile sources (ARB, 1991b). Because there is no species profile for this source, the staff applied an emission rate for non-catalyst, gasoline fueled, on-road motor vehicles to gasoline combustion sources. A 1,3-butadiene emission factor of 0.97 weight percent of total organic gas (TOG) (or 9.7 tons of 1,3-butadiene per thousand tons of TOG) for non-catalyst, gasoline-fueled vehicles was developed by the MSD (ARB, 1991a). The staff estimates 1,3-butadiene emissions statewide from gasoline combustion of other mobile sources as follows:

$$EMS_{Gas} = TOG_{Gas} \times ER_{Gas}$$

Where:

EMS_{Gas}: Statewide 1,3-butadiene emissions from gasoline combustion of other mobile sources (tons per year).

TOG_{Gas}: Statewide estimate of Total Organic Gas from gasoline combustion of other mobile sources (tons per year).

ER_{Gas}: Emission rate of 1,3-butadiene relative to TOG (expressed as 9.7 tons of 1,3-butadiene per thousand tons of TOG).

Substituting the values of TOG_{Gas} and ER_{Gas} the equation becomes:

$$EMS_{Gas} = \frac{83{,}580 \text{ Tons of TOG}}{\text{Year}} \times \frac{9.7 \text{ Tons 1,3-butadiene}}{1000 \text{ Tons TOG}}$$

$$EMS_{Gas} = \frac{811 \text{ Tons 1,3-butadiene}}{\text{Year}}$$

3. <u>Diesel Combustion</u>

There are an estimated 32,081 tons per year of total organic gas (TOG) emitted statewide from diesel combustion of other mobile sources (ARB, 1991b). Because there is no speciation profile for this source, the staff applied an emission rate for diesel on-road motor vehicles to diesel combustion sources. An emission rate of 9.0 mg of butadiene per gram of TOG from diesel vehicular exhaust was estimated (ARB, 1991a). Using this emission rate, the staff estimates 1,3-butadiene emissions statewide from diesel combustion of other mobile sources as follows:

$$EMS_{Die} = TOG_{Die} \times ER_{Die}$$

Where:

EMS_{Die}: Statewide 1,3-butadiene emissions from diesel combustion of other mobile sources (tons per year).

TOG_{Die}: Statewide emissions of Total Organic Gas from diesel combustion of other mobile sources (tons per year).

ER_{Die}: Emission rate of 1,3-butadiene relative to TOG (expressed as 9.0 tons of 1,3-butadiene per thousand tons of TOG).

Substituting the value of TOG_{Die} and ER_{Die} the equation becomes:

$$EMS_{Die} = \frac{32{,}081 \text{ Tons TOG}}{\text{Year}} \times \frac{9.0 \text{ Tons 1,3-butadiene}}{1000 \text{ Tons TOG}}$$

$$EMS_{Die} = \frac{289 \text{ Tons 1,3-butadiene}}{\text{Year}}$$

4. <u>Total Emissions Statewide for Other Mobile Sources</u>

$$EMS_{Tot} = EMS_{Dis} + EMS_{Gas} + EMS_{Die}$$

Where:

EMS_{Tot}: Statewide 1,3-butadiene emissions from all other mobile sources (tons per year).

EMS_{Dis}: Statewide 1,3-butadiene emissions from distillate oil combustion of other mobile sources (tons per year).

EMS_{Gas}: Statewide 1,3-butadiene emissions from gasoline combustion of other mobile sources (tons per year).

EMS_{Die}: Statewide 1,3-butadiene emissions from diesel combustion of other mobile sources (tons per year).

Substituting the value of EMS_{Dis}, EMS_{Gas}, and EMS_{Die} the equation becomes:

$$EMS_{Tot} = \frac{45.98 \text{ Tons}}{\text{Year}} + \frac{811 \text{ Tons}}{\text{Year}} + \frac{289 \text{ Tons}}{\text{Year}}$$

$$EMS_{Tot} = \frac{1{,}146 \text{ Tons 1,3-butadiene}}{\text{Year}}$$ or approximately 1,100 tons per year.

C. FUEL COMBUSTION (STATIONARY POINT SOURCES)

Sources of fuel combustion include boilers, heaters, internal combustion engines, and turbines. Emissions of 1,3-butadiene from fuel combustion sources are based on total organic gas (TOG) emissions from each of three types of fuels (ARB, 1989d), speciation profile (distillate oil), and emission rates (diesel and gasoline) of 1,3-butadiene. The emissions are separately estimated and then added together for the statewide estimate. The staff estimates statewide emissions from fuel combustion sources to be approximately 35 tons of 1,3-butadiene per year.

1. Distillate Oil Combustion

The Air Resources Board's Speciation Manual (ARB, 1989b), contains species profiles by processes. The Speciation Manual lists 1,3-butadiene as a compound contained in Profile #9: Industrial Combustion Engine-Distillate Oil. The weight fraction of 1,3-butadiene is listed as .0590 in this profile. In the absence of a specific profile for boilers, heaters, and turbines using distillate oil, the staff applied profile #9 for internal combustion engines to all the distillate oil combustion sources.

There are an estimated 518.9 tons per year of total organic gas (TOG) emissions statewide from distillate oil combustion (ARB, 1989d). Emissions from residual oil combustion are also included in this statewide estimate. The staff estimated 1,3-butadiene emissions statewide from distillate oil combustion as follows:

$$EMS_{Dis} = TOG_{Dis} \times W_{Dis}$$

Where:

EMS_{Dis}: Statewide 1,3-butadiene emissions from distillate oil combustion sources (tons per year).

TOG_{Dis}: Statewide emissions of Total Organic Gas from distillate oil combustion sources (tons per year).

W_{Dis}: Weight fraction of 1,3-butadiene to Total Organic Gas from distillate oil combustion sources.

Substituting the values of TOG_{Dis} and W_{Dis}, the equation becomes:

$$EMS_{Dis} = \frac{518.9 \text{ Tons TOG}}{\text{Year}} \times \frac{.0590 \text{ Tons of 1,3-butadiene}}{\text{Ton of TOG}}$$

$$EMS_{Dis} = \frac{30.6 \text{ Tons of 1,3-butadiene}}{\text{Year}}$$

2. <u>Gasoline Combustion Sources</u>

There is an estimated 395.5 tons per year of total organic gas (TOG) emissions statewide from gasoline combustion sources (ARB, 1989d). Because there is no species profile for this source, the staff applied an emission rate for non-catalyst, gasoline-fueled, on-road motor vehicles to gasoline combustion sources. An emission rate of 9.7 mg of butadiene per gram of TOG from gasoline vehicular exhaust was estimated (ARB, 1991a). Using this emission rate, the staff estimates 1,3-butadiene emissions statewide from gasoline combustion sources as follows:

$$EMS_{Gas} = TOG_{Gas} \times ER_{Gas}$$

Where:

EMS_{Gas}: Statewide 1,3-butadiene emissions from gasoline combustion sources (tons per year).

TOG_{Gas}: Statewide estimate of Total Organic Gas for gasoline combustion sources (tons per year).

ER_{Gas}: Emission rate of 1,3-butadiene relative to TOG (expressed as 9.7 tons of 1,3-butadiene per thousand tons of TOG).

Substituting the values of TOG_{Gas} and ER_{Gas} the equation becomes:

$$EMS_{Gas} = \frac{395.5 \text{ Tons of TOG}}{\text{Year}} \times \frac{9.7 \text{ Tons 1,3-butadiene}}{1000 \text{ Tons TOG}}$$

$$EMS_{Gas} = \frac{3.84 \text{ Tons 1,3-butadiene}}{\text{Year}}$$

3. <u>Diesel Combustion Sources</u>

There are an estimated 23.9 tons per year of total organic gas (TOG) emissions statewide from diesel combustion sources (ARB, 1989d). Because there is no species profile for this source, the staff applied an emission rate for diesel on-road motor vehicles to diesel combustion sources. An emission rate of 9.0 mg of butadiene per gram of TOG from diesel vehicular exhaust was estimated (ARB, 1991a). Using this emission rate, the staff estimates 1,3-butadiene emissions statewide from diesel combustion sources as follows:

$$EMS_{Die} = TOG_{Die} \times ER_{Die}$$

Where:

EMS_{Die}: Statewide 1,3-butadiene emissions from diesel combustion sources (tons per year).

TOG_{Die}: Statewide Total Organic Gas emissions from diesel combustion sources (tons per year).

ER_{Die}: Emission rate of 1,3-butadiene relative to TOG (expressed as 9.0 tons of 1,3-butadiene per thousand tons of TOG).

Substituting the value of TOG_{Die} and ER_{Die} the equation becomes:

$$EMS_{Die} = \frac{23.9 \text{ Tons TOG}}{\text{Year}} \times \frac{9.0 \text{ Tons 1,3-butadiene}}{1000 \text{ Tons TOG}}$$

$$EMS_{Die} = \frac{.22 \text{ Tons 1,3-butadiene}}{\text{Year}}$$

4. <u>Total Emissions Statewide for Combustion Sources</u>

$$EMS_{Tot} = EMS_{Dis} + EMS_{Gas} + EMS_{Die}$$

Where:

EMS_{Tot}: Statewide 1,3-butadiene emissions from all combustion sources (tons per year).

EMS_{Dis}: Statewide 1,3-butadiene emissions from distillate oil combustion sources (tons per year).

EMS_{Gas}: Statewide 1,3-butadiene emissions from gasoline combustion sources (tons per year).

EMS_{Die}: Statewide 1,3-butadiene emissions from diesel combustion sources (tons per year).

Substituting the value of EMS_{Dis}, EMS_{GAs}, and EMS_{Die} the equation becomes:

$$EMS_{Tot} = \frac{30.6 \text{ Tons}}{\text{Year}} + \frac{3.84 \text{ Tons}}{\text{Year}} + \frac{.22 \text{ Tons}}{\text{Year}}$$

$$EMS_{Tot} = \frac{34.66 \text{ Ton 1,3-butadiene}}{\text{Year}}$$ or approximately 35 tons per year.

D. PETROLEUM REFINING

The Bay Area Air Quality Management District (BAAQMD) reports 6,200 lbs (3.1 tons) of 1,3-butadiene emissions from the five refineries in their jurisdiction (BAAQMD, 1989a). These five refineries have a total design capacity of 807,900 barrels (bbl) of crude oil per stream day (Oil & Gas, 1989). Total design capacities for all 31 refineries in the state is 2,416,930 bbl per stream day.

Assuming the refineries in other parts of the state would emit 1,3-butadiene similar to the Bay Area facilities, the staff estimates 1,3-butadiene emissions statewide as follows:

$$EMS = EMS_{BA} \times R$$

Where:

EMS: Statewide 1,3-butadiene emissions from refineries (tons per year).

EMS_{BA}: 1,3-butadiene emissions from refineries in the Bay Area (tons per year).

R: Ratio of design capacities of statewide refineries to design capacities of Bay Area refineries.

Substituting the values of EMS_{BA} and R, the equation becomes:

$$EMS = \frac{3.1 \text{ tons of 1,3 Butadiene}}{\text{Year}} \times \frac{2{,}416{,}930 \text{ bbl crude oil/day}}{807{,}900 \text{ bbl crude oil/day}}$$

EMS = 9.27 or approximately 9 tons per year.

E. FUEL COMBUSTION (STATIONARY AREA SOURCE)

The area source of fuel combustion includes agricultural sources, oil and gas production, manufacturing and industrial, services and commerce, and residential area sources. Emissions of 1,3-butadiene from fuel combustion area sources are based on total organic gas (TOG) emissions for each of two types of combustion fuels (ARB, 1989a), speciation profile (distillate oil), and emission rate (diesel) of 1,3-butadiene. The emissions are separately estimated and then added together for the statewide estimate. The staff estimates statewide emissions from fuel combustion area sources to be approximately 110 tons of 1,3-butadiene per year.

1. Distillate Oil Combustion

The Air Resources Board's Speciation Manual (ARB, 1989b), contains species profiles by processes. The Speciation Manual lists 1,3-butadiene as a compound contained in Profile #9: Industrial Internal Combustion Engine-Distillate Oil. The weight fraction of 1,3-butadiene is listed as .0590 in this profile. In the absence of a specific profile for the sources listed above using distillate oil, the staff applied profile #9 for internal combustion engines to all the distillate oil combustion sources.

There is an estimated 1,473.90 tons per year of total organic gas (TOG) emissions statewide for distillate oil combustion area sources (ARB, 1989a). Emissions from residual oil combustion are also included in this statewide estimate. The staff estimated 1,3-butadiene emissions statewide for distillate oil combustion area sources as follows:

$$EMS_{Dis} = TOG_{Dis} \times W_{Dis}$$

Where:

EMS_{Dis}: Statewide 1,3-butadiene emissions from distillate oil combustion area sources (tons per year).

TOG_{Dis}: Statewide emissions of Total Organic Gas from distillate oil combustion area sources (tons per year).

W_{Dis}: Weight fraction of 1,3-butadiene to Total Organic Gas from distillate oil combustion area sources.

Substituting the values of TOG_{Dis} and W_{Dis}, the equation becomes:

$$EMS_{Dis} = \frac{1{,}473.90 \text{ Tons TOG}}{\text{Year}} \times \frac{.0590 \text{ Tons of 1,3-butadiene}}{\text{Ton of TOG}}$$

$$EMS_{Dis} = \frac{86.96 \text{ Tons of 1,3-butadiene}}{\text{Year}}$$

2. Diesel Combustion

There are an estimated 2,417.61 tons per year of total organic gas (TOG) area emissions statewide from diesel combustion (ARB, 1989a). Because there is no species profile for this source, the staff will apply an emission rate for diesel on-road motor vehicles to diesel combustion sources. An emission rate of 9.0 mg of butadiene per gram of TOG from diesel vehicular exhaust was estimated (ARB, 1991a). Using this emission rate, the staff estimates 1,3-butadiene area emissions statewide from diesel combustion as follows:

$$EMS_{Die} = TOG_{Die} \times ER_{Die}$$

Where:

EMS_{Die}: Statewide 1,3-butadiene emissions from diesel combustion area sources (tons per year).

TOG_{Die}: Statewide estimate of Total Organic Gas from diesel combustion area sources (tons per year).

ER_{Die}: Emission rate of 1,3-butadiene relative to TOG (expressed as 9.0 tons of 1,3-butadiene per thousand tons of TOG).

Substituting the value of TOG_{Die} and ER_{Die} the equation becomes:

$$EMS_{Die} = \frac{2{,}417.61 \text{ Tons TOG}}{\text{Year}} \times \frac{9.0 \text{ Tons 1,3-butadiene}}{1000 \text{ Tons TOG}}$$

$$EMS_{Die} = \frac{21.76 \text{ Tons 1,3-butadiene}}{\text{Year}}$$

3. Total Emissions Statewide for Fuel Combustion Area Sources

$$EMS_{Tot} = EMS_{Dis} + EMS_{Die}$$

Where:

EMS_{Tot}: Statewide 1,3-butadiene emissions from all area sources involving fuel combustion (tons per year).

EMS_{Dis}: Statewide 1,3-butadiene emissions from area sources involving distillate oil combustion (tons per year).

EMS_{Die}: Statewide 1,3-butadiene emissions from area sources involving diesel combustion (tons per year).

Substituting the value of EMS_{Dis} and EMS_{Die} the equation becomes:

$$EMS_{Tot} = \frac{86.96 \text{ Tons}}{\text{Year}} + \frac{21.76 \text{ Tons}}{\text{Year}}$$

$$EMS_{Tot} = \frac{108.72 \text{ Ton 1,3-butadiene}}{\text{Year}}$$ or approximately 110 tons per year.

References for Appendix A

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Appendix B

Standard Operating Procedure for the Determination of 1,3-Butadiene in Ambient Air

SUMMA Polished Canister Method (Current SOP) ..... B-1 to B-14

Tedlar Bag Method (Previous SOP) ..... B-15 to B-27

CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

S.O.P. No. MLD 013

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF 1,3-BUTADIENE IN AMBIENT AIR

1. SCOPE

This document describes a procedure for the sampling and analysis of 1,3-butadiene at concentrations normally found in ambient air. This procedure was developed by NLB staff.

2. SUMMARY OF METHOD

Ambient air is continuously sampled into a stainless steel SUMMA polished canister and immediately sent to the NLB organics laboratory for analysis. A 200ml sample is drawn from the canister through a Carbotrap C preconcentration system to trap the hydrocarbons with subsequent thermal desorption to the gas chromatograph for analysis. The C_2 to C_4 saturated and unsaturated hydrocarbons are separated by a packed column and temperature programming. The components eluting from the column are detected by photoionization (PID) and flame ionization detectors (FID) and quantitated by comparisons to standards. The 1,3-butadiene is identified based on retention times and confirmation is accomplished by the use of a second detector, FID.

3. INTERFERENCES/LIMITATIONS

3.01 Compounds having similar GC retention times may interfere, causing misidentification or faulty quantitation.

3.02 Although preliminary studies have shown that 1,3-butadiene can be considered stable in stainless steel canisters, every effort must be made to analyze the sample as soon as possible. Extreme care should be taken to prevent contamination during sample collection, transportation and subsequent analysis.

3.03 Although the analytical system will separate and detect saturated and other unsaturated hydrocarbons, 1,3-butadiene is the only compound addressed by this procedure.

3.04 The FID is used as a confirmation detector for results greater than 10X the PID detection limit. No results are reported from this detector. It should be monitored for possible coeluting compounds and ambiguous results from the PID.

3.05 Not more than 10 samples should be run consecutively without recalibration due to PID lamp window hazing causing decreased sensitivity. The lamp should be cleaned when the signal decreases substantially.

3.06 Butadiene standards are unstable and have been found to degrade. NIST standards should be ordered frequently to monitor older standards. (Butadiene stability is estimated at approximately six months) A comparison of butadiene response to another stable compound in the calibration cylinder should be made. A change in the butadiene/isoprene ratio in the cylinder will indicate degradation of butadiene in the calibration standard.

3.07 When running dual method using the DS 654 data system the WI should be the same for the two methods or it will cause the data system to lockup, and loss of data will occur.

3.08 Increased background noise could be caused by a buildup of high boiling compounds in the detector. To reduce this noise the detector temperature can be increased to 280°C followed by lamp cleaning or disassembly of the PID chamber and cleaning with an erasure and methanol.

3.09 Daily baseline shifting may be caused from high boiling compounds not eluting from the column due to the low column limit. The column should be baked out after each set of analytical runs to remove the higher boiling compounds from the column.

3.10 Vinyl chloride is monitored by this method but not reported due to the low breakthrough volume and low ambient concentration.

3.11 Isoprene is monitored by this method but not reported due to poor baseline and interfering peaks in the later portion of the chromatogram.

4. <u>APPARATUS</u>

4.01 Varian Model 6000 Gas Chromatograph equipped with a 10.2 ev PID and FID, a 10' x 2 mm i.d. glass column packed with 0.19 percent picric acid on 80/100 Carbopack C, and a Vista 654 Data Station.

4.02 Varian Vista 654 data system used for GC and autosampler control.

4.03 Nelson 2600 data station. IBM PS-2 model 30 based. Used for data collection and integration.

4.04 A preconcentration system equipped with a Carbotrap and automated sampling valve.

4.05 Porter mass flow controller 50 or 100cc/min calibrated in the 50 cc/minute range.

4.06 House vacuum system capable of drawing greater than 50cc/min.

4.07 16-port autosampling valve equipped with a low volume regulator.

4.08 3-way automated valve capable of being controlled externally and equipped with a particulate filter.

5. REAGENTS

NIST standard with 1,3-Butadiene and Isoprene. A control cylinder containing 1,3-Butadiene at a concentration determined using the NIST cylinder. The Isoprene will be used as an internal standard to monitor the degradation of 1,3-butadiene in the NIST standard.

6. PROCEDURE

6.01 Initial Set Up

6.01.01 Connect samples to the autosampler and purge the autosampler lines.

6.01.02 Set up appropriate number of samples in the Varian 654 data system to sequence through the samples and methods. (See Appendix II.)

6.01.03 Set up Nelson 2600 data system to receive data for integration. (See Appendix III.)

6.02 Sample Preconcentration

6.02.01 The Carbotrap preconcentration system is shown in Figure I.

6.02.02 Standards and ambient samples are introduced to the GC from the automated preconcentration system. The sample is selected by the autosampler and passes through the pressure regulator set at zero (with flow).

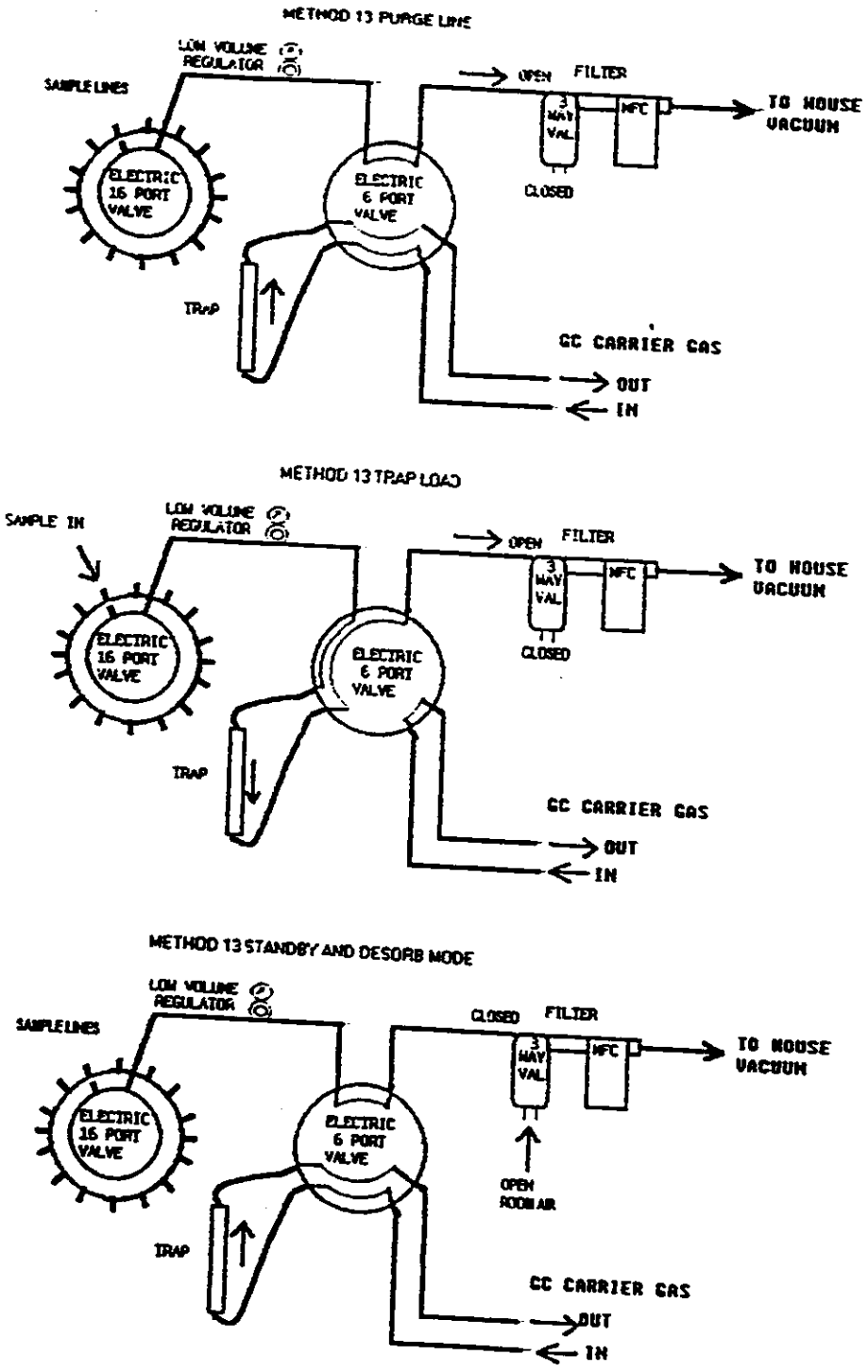
6.02.03 A three way valve is automatically opened 1 min before loading the trap to purge the lines and regulator with the current sample. The flow is controlled by a mass flow controller connected to house vacuum.

6.02.04 The sampling valve is then cycled to divert the flow of sample through the trap. After 200 cc (4 min) of sample has been trapped the valve cycles back to divert the column flow through the trap. The carrier gas travels in a direction opposite of the sample flow.

6.02.05 The desorption of the trapped 1,3-butadiene and other sample components is automatically initiated for a 4 min period at 180 C. The compounds are transferred to the head of the GC column for subsequent analysis.

Figure 1

PRECONCENTRATION SYSTEM



6.02.06 The 16-port valve is advanced at the end of the sampling period to the next sample. The three way valve is closed to reduce loss of the next sample.

6.03 Analysis

6.03.01 The preconcentrated sample is separated under the chromatographic conditions listed below. The resulting chromatogram (Figure 2) is then integrated and quantitated by reference to calibration standard gases.

6.03.02 Instrument Conditions:

GC: Column: 10' x 2 mm i.d. glass column, packed with 80/100 Carbopack C/0.19 percent picric acid

Temperatures: Injector: 150°C
Detector: 250°C
Oven: 40°C, hold for 9 min.,
3°C /min ramp to 70°C, hold for 0 min
20°C/min ramp to 115°C, hold for 13.75 min.

Flow Rate: Carrier: N_2, 30 cc/min.
H_2, 30 cc/min.
Air, 240 cc/min

Detector: PID: Range X1, 10.2 ev lamp

FID: Range X 10^{-12}

Concentrator: Carbotrap: Sampling: 4 min. at 50 cc/min. (25°C)
Desorb: 4 min. at 30 cc/min. (180°C)

Time Relays:

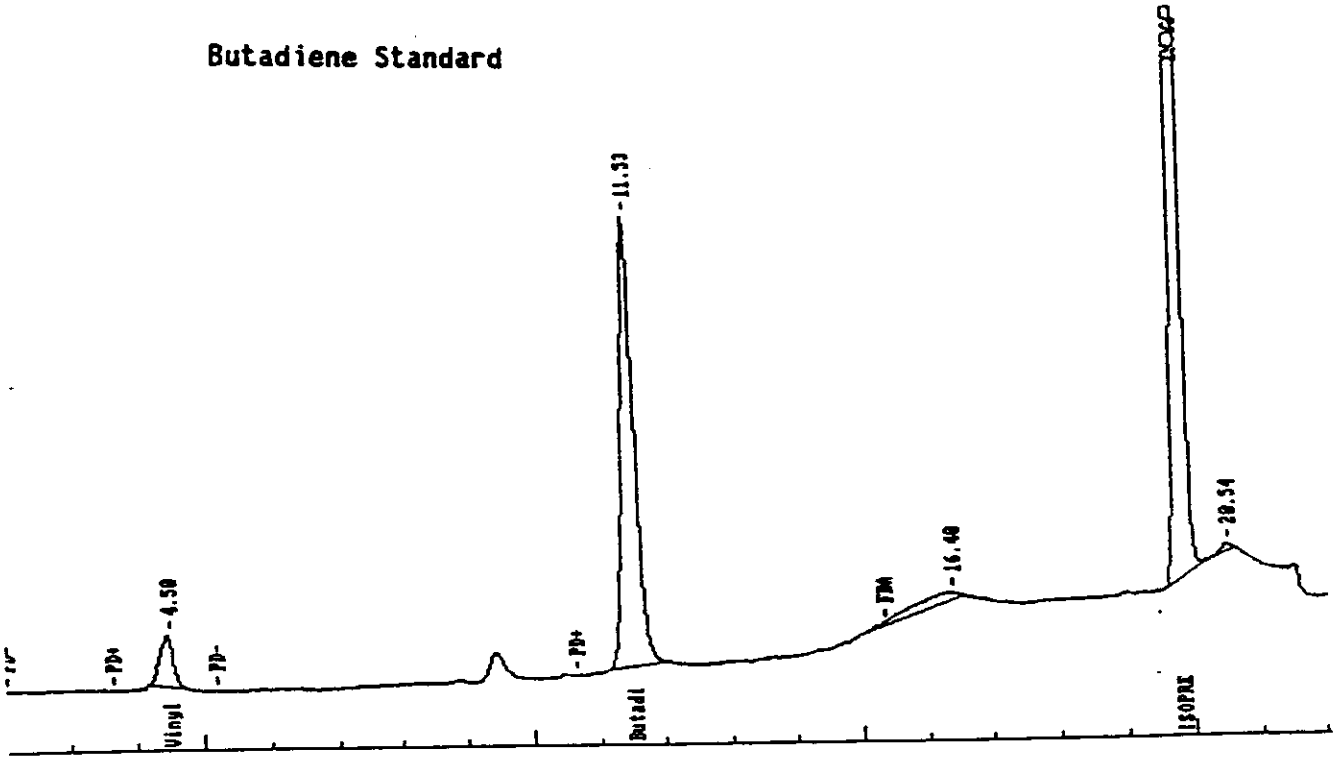
Line#	Time(min)	On	Off
1	0.00		23458
2	0.01	5	
3	1.00	2	
4	5.00	348	25
5	5.08		38
6	9.00		4

Time Relay Functions

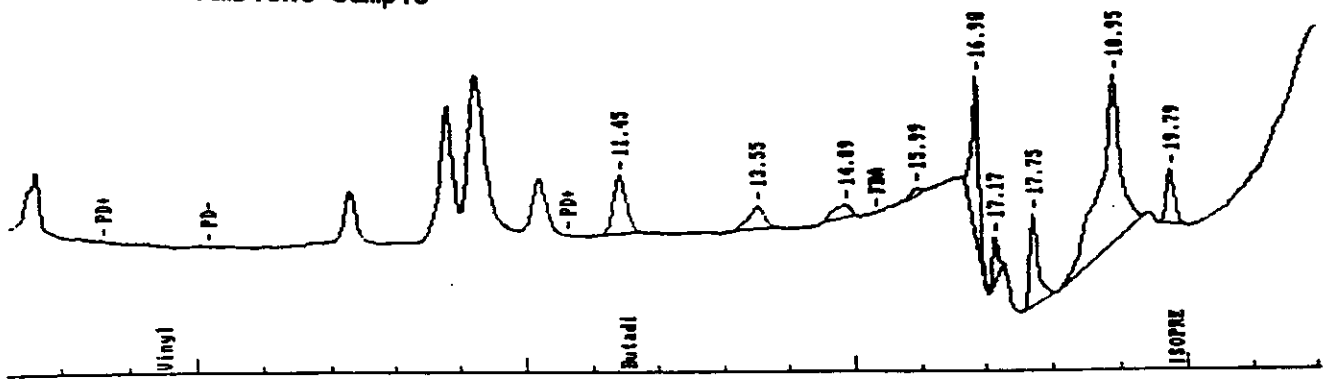
relay 2 advances valve to load trap
relay 3 (a) returns valve for desorption of trapped compounds
(b) advances autosampler to next sample
(c) sends start signal to 2600 data system
relay 4 controls trap thermal desorption
relay 5 controls three way solenoid valve for line purging and sampling
relay 8 alarm

Figure 2

Butadiene Standard



Ambient Sample



6.03.03 Prior to instrument calibration, a zero air must be analyzed to detect instrument or sampling contamination. The zero air analysis must be free of interfering peaks. System blanks must also be run after any sample which contains high concentrations (>4 ppb) of 1,3-butadiene to detect possible carry-over.

6.03.04 System calibration is performed daily by passing 200cc of a primary or secondary NIST traceable standard of a concentration not greater than 2ppb. Attention must be given to trends in response factor values which may indicate instrument, standard or detector sensitivity changes.

6.03.05 A control cylinder is then analysed to assess the calibration and first sample analysis. The results of the control cylinder must fall within 3 standard deviations of the assigned value determined from the standard.

6.03.06 Ambient samples are introduced in the same manner as the calibration and control standards. The resultant peaks are identified by retention times and quantified relative to the calibration standard.

6.03.07 Multipoint calibrations are conducted every three months. Each multipoint calibration consists of a system blank and at least three different concentrations of the standard performed in triplicate. If data indicate that the analyses are consistently unacceptable, more frequent multipoint calibrations may be required.

7. PERFORMANCE

7.01 Duplicate analyses are performed on 10 percent of all ambient samples received from the field. The relative percent difference of the duplicate analyses are recorded and included in the monthly Quality Control report. Only those data for concentrations in excess of the quantitation limits (0.04 ppb for 1,3-butadiene) are reported.

7.02 The results of the daily control standard analyses are plotted on the Method Control Chart. Warning and control limits are established from historical data to track analytical trends. The warning limit is two times the method standard deviation and the control limit is three times the method standard deviation.

7.03 If the control results continuously fall outside the warning limit the instrumentation should be checked thoroughly for any instrumentation problems.

7.04 If the results from the control cylinder are out of the control limits no data shall be reported for that run. The standard and control cylinder should be reanalysed prior to ambient sample analysis.

7.05 The FID which is connected second in series to the PID will be used as a confirmation check for butadiene.

8. METHOD SENSITIVITY, PRECISION AND ACCURACY

8.01 Linearity is determined by multipoint analysis. The detection limit and correlation are derived from this analysis and listed in table 1.

Table 1.

Vinyl Chloride
R squared = 0.6326 (Breakthrough volume)
LOD = Not calculated
Amount = 1.4004E-03 * Area + -2.994

Butadiene
R squared = 1.0000
LOD = 0.044 ppb
Amount = 3.0656E-05 * Area + 4.0699E-02

Isoprene
R squared = 0.9998
LOD = 0.15 ppb
Amount = 3.2687E-05 * Area + 1.0606E-01

The method used to calculate the limit of detection is
LOD = Intercept + 3(RSD of lowest std.)*Intercept

8.02 The breakthrough volume for vinyl chloride is less than 200 cc. For butadiene and isoprene the breakthrough volume is greater than 400 cc.

APPENDIX I

BUTADIENE STANDARD
NIST 9005

Cylinder NIST 9005 is the current cylinder being used for the calibration of method 013. This is the latest cylinder available for butadiene. This cylinder has not been certified for butadiene due to the known instability, however this represents the best source available for instrument calibration.

COMPOUND	CONCENTRATION
Vinyl Chloride	2.0 +/- 0.1 ppb
Butadiene	1.2 ppb (not certified)
Isoprene	2.1 +/- 0.2 ppb

APPENDIX II
VARIAN 654 DATA SYSTEM

The Varian 654 data system is currently being used as method sequencer, sample sequencer and backup data system. It is equipped with the interactive graphics integration software. The 654 is used because of the lack of control of the instrumentation in the Nelson 2600 software.

AUTOMATION

The Varian 654 controls the automation system. This includes the GC parameters, the automation events, and the different methods used for the butadiene analysis.

In the automodify (AM) mode yes is selected for self start. The current methods used are Bakeout, Buta, and Autoend.

Bakeout is a ten minute run that bakes out the trap for five minutes and the GC for ten minutes. This is used prior to the analysis each day.

Buta is a dual method that synchronizes the PID and FID methods. M1A is the current PID primary method. M1B is the FID secondary method. In method M1A be sure in section 9 that the sample list contains the correct number of samples for the day. Be sure method M1B has the correct number of samples or more. The automation will only run as many times as the least number of samples in the method lists.

Autoend is the last method in the method list. This is a bakeout method that begins after all of the samples have been run.

To initiate an automated run with the 654 use the autostart (AS) command. The sequence line determines which method is selected, 1 is bakeout, 2 is buta, and 3 is autoend. Method sample list line is which sample in the sample list is selected within the current method. Inject should usually be 1 when started, this is related to where the method is started. For more information on the data system use the DS-650 Series Data System Operator's Reference Manual.

INTERACTIVE GRAPHICS

Interactive graphics can be used to backup the Nelson system in case the Nelson system is inoperable for any reason. A brief description of some of the vague topics in the manual will be covered below.

To use the interactive graphics (IG), first a file known as a graphics data set must be saved from a raw data file. This can be done in two ways. In section 7 of the method save file must be chosen, GDS type. Now a GDS file can be saved during a normal run or by performing a recalculation of a raw data file (RF) and selecting yes for the save file per method option. Either of these methods may be used to generate a GDS file.

To select items in the interactive graphics use the arrow keys and the spacebar.

For more information on the interactive graphics use the DS-650 Series Data System Software Options Manual.

MULTIPOINTS

Multipoint analysis can be performed more easily using the Varian 654 to sequence through methods that change the sampling time. The methods currently used are MULTI 50, MULTI 100, MULTI 200, MULTI 300, AND MULTI 400. The methods reduce the sampling time by opening the sampling valve at a later time and holding the thermal desorption at a constant time to maintain the same retention time. Connect the standard that will be used for the multipoint analysis to the displayed port. Change the AUTO ADVANCE switch on the autosampler to the OFF position to hold the autosampler in one position. Perform auto modify (AM) and put the multi methods (listed above) in the desired sequence. Set up the Nelson 2600 to receive the data for integration and calculation. Initiate an autostart (AS) to begin the multipoint analysis.

REFERENCES:

DS-650 Series Data System Operators Manual, Volume 1, Varian Associates, Inc., 1988, Publication Number 03-914182-00

DS-650 Series Data System Software Options Manual, Volume 2, Varian Associates, Inc., 1988, Publication Number 03-914183-00

APPENDIX III
NELSON 2600 DATA SYSTEM

NELSON DATA SYSTEM: The Nelson 2600 is a software based menu driven system. The Nelson set-up information is presented below:

Method BUTA and CUTA
Sequence File Name BUTA
Interface Number 1
The file naming procedure for the Nelson 2600 system is presented below.

BASE NAME

The users of the Nelson 2600 system are given 5 characters to form the base name. Data is stored using this base name. The cycle of injection number is appended to the selected base name and the data files are stored on the specified drive. The same base name is used for storing raw, area and header files, but the three character extension differentiates one file from another. If a duplicate file name exists the system will rename the current sample. This can and will cause problems with LIMS transfer procedures. To prevent this and to allow easy identification of data, the following convention will be used for naming Nelson files.

1. Use only a 5 character base name for data runs.
2. The first two characters will be a month code.
3. The third and fourth characters will be a date code.
4. The fifth character will be an instrument code.
5. The sixth through eighth character is automatically assigned by the Nelson system and represents the sample number for the base name.

MONTH CODES

JAN = JA	JUL = JU
FEB = FB	AUG = AU
MAR = MR	SEP = SE
APR = AP	OCT = OC
MAY = MA	NOV = NO
JUN = JN	DEC = DE

INSTRUMENT CODES

METHOD 002 = A
METHOD 002A = B
METHOD 012 = C
METHOD 013 = D

EXAMPLE: MA08A WOULD BE MAY 8TH ON METHOD 002A

SAMPLE NAME FORMAT:

Within a sequence or during a manual download you must enter a sample name. The format for this is as follows.

Generally a system blank or sample of zero air is run as the first sample of the day to insure that the system is free of contamination.

Enter a zero air sample as: Zero Air.

Enter a system blank as: System Blank .

After the zero air, a calibration standard is run. If you wish to automatically update the calibration factors put a ^ symbol in the Nelson sample list at the end of the sample name. For example:

NIST 9005^1AV (for a level 1 average of calibration factors)

or

NIST 9005^1RE (for a level 1 replacement of calibration factors)

Samples that have been logged into LIMS and that will be transferred will use the first 6 characters for the LIMS number. The LIMS number itself will be limited to 5 characters and the 6th character is used as a replicate code. If this is left blank it represents the first replicate. A-J represents the 2nd through 10th replicates. The first character must be 0, 1 or 2 for LIMS to recognize this as a LIMS number. If the LIMS number is 90003458 use 03458 as the Nelson code. After the first 6 characters, enter in a space and then type in the sample location or other information. For example the first replicate of a Modesto sample having a LIMS number of 02345 would be entered as:

02345A Modesto

If the sixth character is not used insert a space after the LIMS number.

The BUTA method is used to call both PID and FID methods. Normally only one GC will be running in the autosample mode. The Nelson system will then sequence the samples and append a number to the root (default file name)

MULTIPOINTS

The combination of the autosampler and the Nelson 2600 data system reduces the task of multipoints from a time consuming ordeal to a easy analysis and calculation. Use method BMPTS in the 2600and connect multipoint standard and select auto advance on the autosampler to the off position. Use the multipoint methods in the varian 654 to control the valve switching. Enter the standards in the 2600 as different level standards.(ex. Nist9005^1AV for the first level; Nist9005^2AV for the second level; Nist9005^3AV for the third level; etc.) Perform a calibration factor update and a plot calibration curve from the 2600 main menu. Calculate LOD from this data.

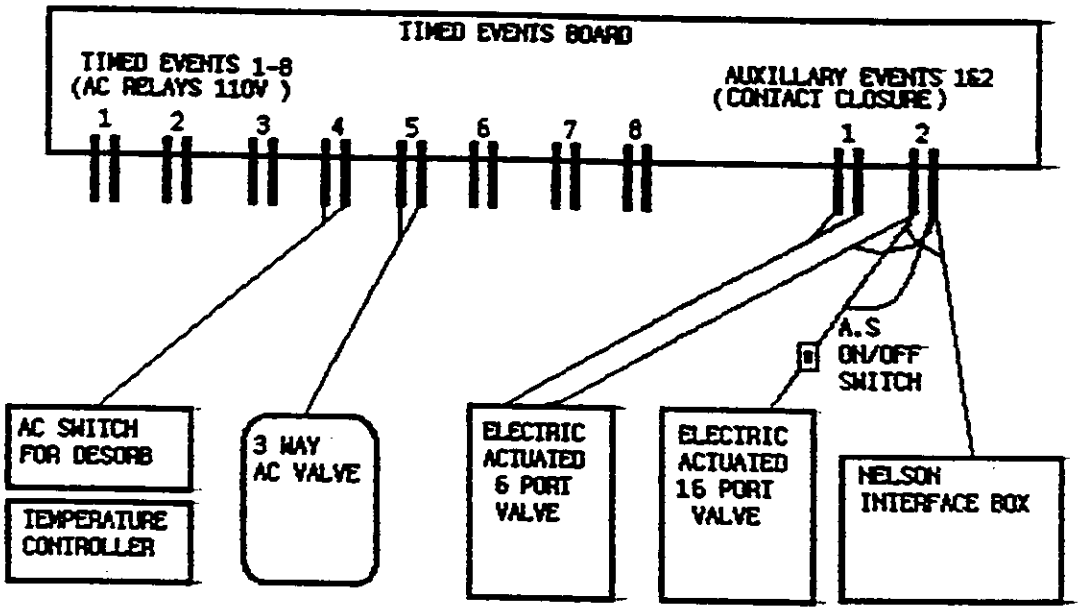
REFERENCES:

S.O.P No. MLD 002, Revision 4.0, 03/01/90

PE NELSON 3000 Series Chromatography Data System Users Manual, 1987, Part Number 68-2600-00

APPENDIX IV
TIMED EVENTS BOARD DIAGRAM

This diagram shows connection of the relays and auxiliary events to the automated devices used for Method 13.



NOTE: AUXILLARY 1 IS ACTUATED WITH EVENT 2
AUXILLARY 2 IS ACTUATED WITH EVENT 3

State of California
Air Resources Board
Monitoring and Laboratory Division

S.O.P. No. NLB013

Standard Operating Procedure for the Determination of 1,3-Butadiene and Vinyl Chloride in Ambient Air

1.0 SCOPE

This document describes a procedure for the sampling and analysis of 1,3-butadiene and vinyl chloride at concentrations normally found in ambient air.

2.0 SUMMARY OF METHOD

After being continuously sampled into a Tedlar bag over a period of 24 hours, ambient air is immediately sent to the laboratory for analysis. A subsample (300 cc) from the bag is passed through a Carbotrap preconcentration system to trap the hydrocarbons with subsequent thermal desorption to the gas chromatograph for analysis. The C_2 to C_4 saturated and unsaturated hydrocarbons are separated by a packed column and temperature programming. The components eluting from the column are detected by photoionization (PID) and flame ionization detectors (FID) and quantitated by comparisons to standards. The 1,3-butadiene and vinyl chloride are identified based on retention times and confirmation is accomplished by the use of a second detector, FID.

3.0 INTERFERENCES/LIMITATIONS

a. Compounds having similar GC retention times may interfere, causing misidentification or faulty quantitation.

b. Although preliminary studies have shown that 1,3-butadiene can be considered stable in Tedlar bags if protected from sunlight, every effort must be made to analyze the sample as soon as possible. Extreme care should be taken to prevent contamination during sample collection, transportation and subsequent analysis. Stability of vinyl chloride in tedlar bags has not been studied in the lab as yet.

c. Although the analytical system will separate and detect saturated and other unsaturated hydrocarbons, 1,3-butadiene and vinyl chloride are the only compounds addressed by this procedure.

d. The FID detects almost all compounds,and may not give accurate values for confirmation results. For now, only those values which are at least 10X the PID LOD and <54% relative error (RE) as obtained from Table 1 will be reported as confirmation values. Other columns and/or GC/MS methods will be investigated in the future.

4.0 APPARATUS

a. Varian Model 6000 Gas Chromatograph equipped with a 10.2 ev PID and FID, a 10' x 2 mm i.d. glass column packed with 0.19 percent picric acid on 80/100 Carbopack C, and a Vista 604 Data Station.

b. A preconcentration system equipped with a Carbotrap and sampling valves.

c. Matheson Model 8240 Mass Flow Controller calibrated in the 5-100 cc/minute range.

d. Laboratory timer, accurate to 0.05 minute.

e. Gas-tight microliter syringes; 5, 10, and 25 ul sizes.

f. Vacuum pump, GAST, with by-pass valving.

5.0 REAGENTS

a. Scott-Marin, Inc. specialty gas tank, 5.21 ppb and 0.94 ppb 1,3-butadiene in high purity nitrogen used as a working standard and a control standard, respectively.

b. Scott-Marin, Inc. Specialty gas mixture containing 10.0 ppb vinyl chloride used as a working standard.

6.0 PROCEDURE

a. Sample Preconcentration

1) The Carbotrap preconcentration system is shown in Figure 1.

Table 1

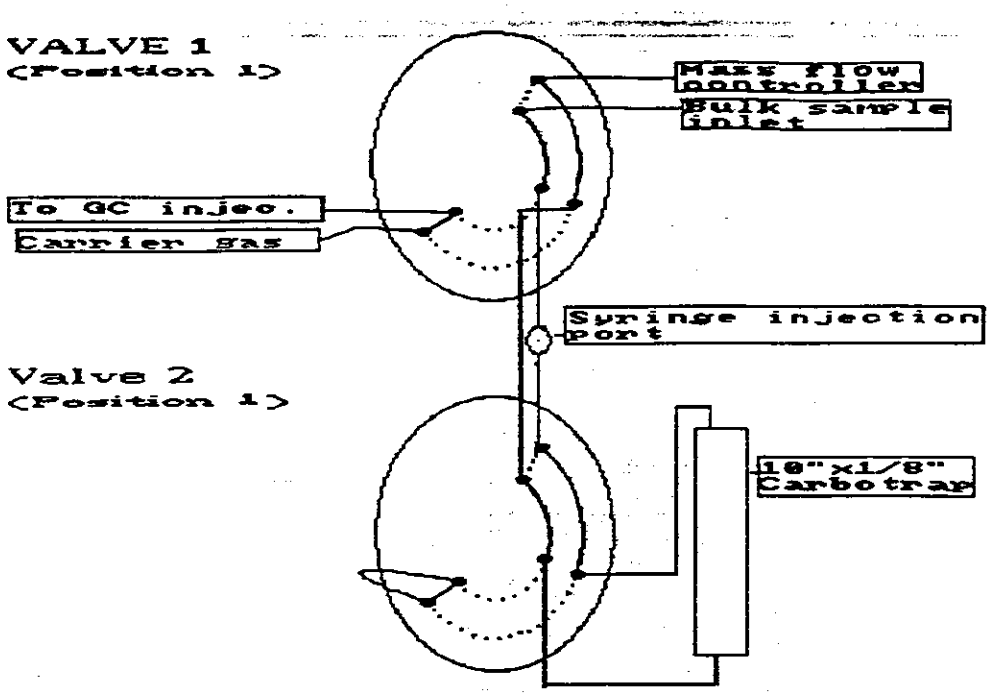
ANALYSIS VALUES OF CYLINDER AAL1728 (0.94 ppb 1,3-BUTADIENE USING PID AND FID

ANALYSIS DATE	PPB 1,3-BUTADIENE PID	FID
10/05/88	0.97	1.03
10/06/88	0.93	1.14
10/07/88	0.90	0.70
10/11/88	0.90	1.18
10/12/88	0.95	0.87
10/13/88	1.0	0.49
10/14/88	0.95	0.61
10/18/88	0.95	0.92
10/27/88	0.82	0.73
10/28/88	0.87	0.88
11/02/88	0.90	1.04
11/03/88	1.02	1.05
11/07/88	0.99	0.80
11/15/88	0.99	0.62
11/17/88	0.73	1.00
11/18/88	0.75	1.29
11/22/88	0.70	1.05
11/23/88	0.94	0.91
11/30/88	0.84	0.60
12/01/88	0.94	0.88
12/06/88	1.05	0.92
12/07/88	0.88	1.16
12/08/88	1.01	0.88
AVERAGE:	0.91	0.90
STD. DEV.:	0.093	0.21
% RSD:	10.2	23.0

AVERAGE BIAS BETWEEN DETECTORS = 1%

Figure 1

PRECONCENTRATION SYSTEM



OPERATIONAL VALVE POSITIONS

Valve 1 Position	Valve 2 Position	Sampling Mode
1	1	Bulk Sampling
2	1	Purge/Desorb
2	2	Trap Isolate

2) High concentration samples and standards are introduced into the preconcentration system through the in-line septum using a gas-tight microliter syringe. The injected sample is swept into the Carbotrap at 25 C with 300 cc of high purity nitrogen (50 cc/minute for six minutes).

3) Ambient samples are introduced from Tedlar bags using a vacuum pump and mass flow controller. The sample is drawn through the Carbotrap at 50 cc/minute for six minutes (300 cc total volume). The 1,3-butadiene and vinyl chloride are concentrated on the trap for later desorption. Similary, standards are introduced directly from the gas cylinders or canisters. Fifty cc of the 5.21 ppb working standard and 100cc of 0.94 ppb standard are used for calibration and control standards. respectively.

4) The carrier gas from the chromatograph is then diverted to the Carbotrap. The carrier gas flows in a direction opposite to the sample flow. The gas chromatograph/data system is started and the Carbotrap heated ballistically to 180 C. The collected hydrocarbons are thermally desorbed from the trap and are swept into the gas chromatographic column.

b. Analysis

1) The preconcentrated sample is separated under the chromatographic conditions listed below. The resulting chromatogram (Figure 2) is then integrated and quantitated by reference to calibration standard gases.

PID and FID chromatograms of vinyl chloride and 1,3-butadiene are shown in Figures 3A, 3B, 4A, and 4B.

2) Instrument Conditions:

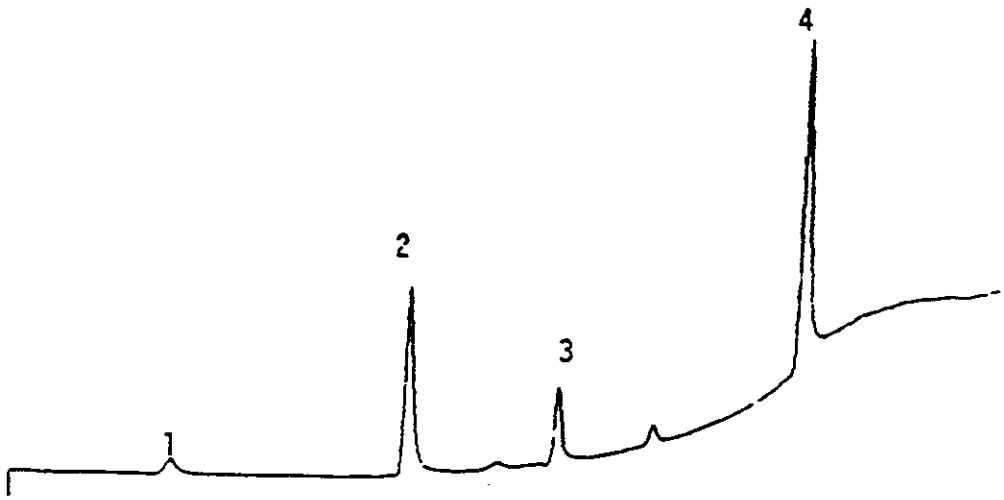
GC: Column: 10' x 2 mm i.d. glass column, packed with 80/100 Carbopack C/0.19 percent picric acid

Temperatures:
- Injector: 150 C
- Detector: 250 C
- Oven: 50 C, hold for 1 min., 4 C/min. ramp to 85 C, hold for 1 min.,10 C/min. ramp to 110 C, hold for 5 min.

Figure 2

CHROMATOGRAM OF AN OLEFIN STANDARD

DETECTOR: 10.2 ev PID
ATTENUATION: 32



LIST OF COMPONENTS

1.	1-Propene	10ppb
2.	1-Butene	10ppb
3.	1,3-Butadiene	2.5ppb
4.	1-Pentene	10ppb

Figure 3A

PID Chromatogram of Vinyl Chloride (0.83 ppb)

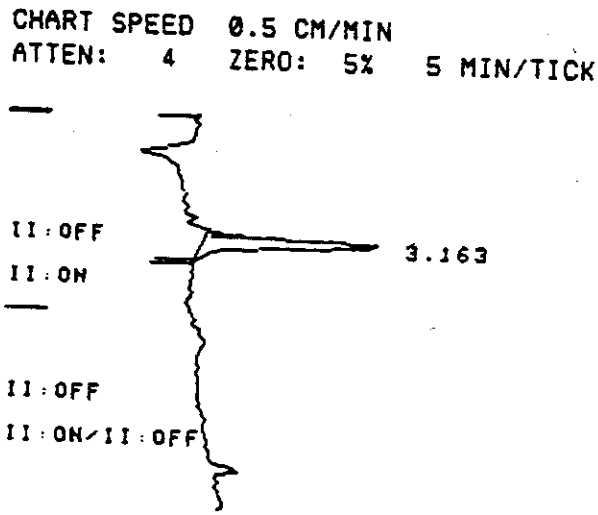


Figure 3B

FID Chromatogram of Vinyl Chloride (0.83 ppb)

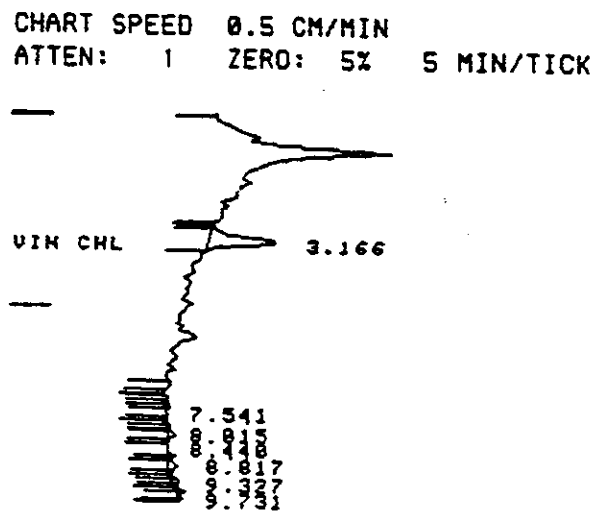


Figure 4A

PID Chromatogram of 1,3-Butadiene (0.31 ppb)

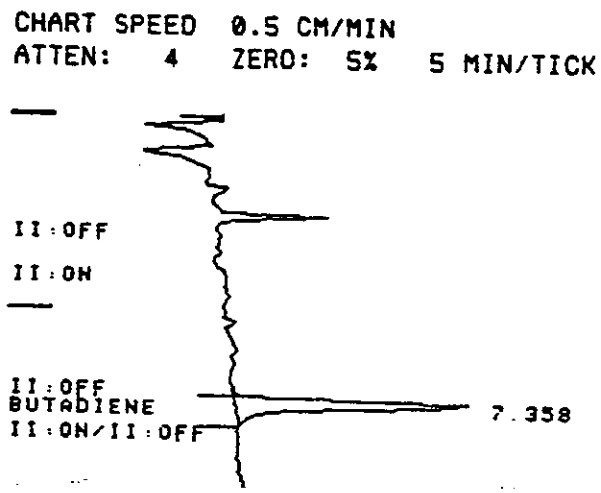
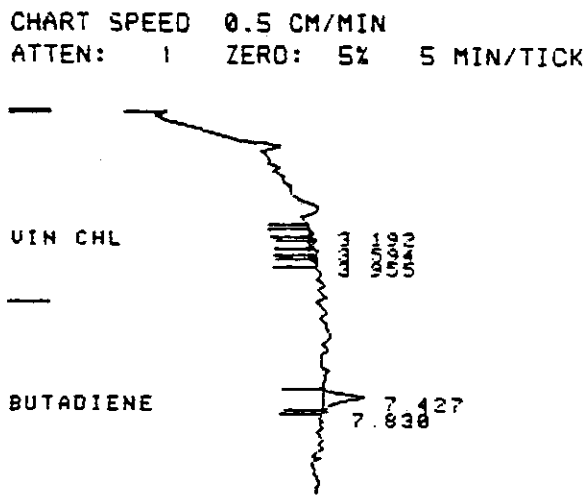


Figure 4B

FID Chromatogram of 1,3-Butadiene (0.87 ppb)



Flow Rate: Carrier: N_2, 20 cc/min.
H_2, 20 cc/min.
Air, 240 cc/min

Detector: PID: Range X1, 10.2 ev lamp

FID: Range X 10^{-12}

Concentrator: Carbotrap: Purge: 0.5 min. at 20 cc/min. (25 C)
Sampling: 6 min. at 50 cc/min. (25 C)
Desorb: 4 min. at 20 cc/min. (180 C)

3) Prior to instrument calibration, a system blank must be analyzed. This is done by trapping 300 cc of purge gas with subsequent desorption and analysis. The system blank analysis must be free of interfering peaks. System blanks must also be run after any sample which contains high concentrations (>4 ppb) of 1,3-butadiene and vinyl chloride to detect possible carry-over.

4) System calibration is performed daily by passing 50 cc (effective concentration of 0.87 ppb) of 5.21 ppb 1,3-butadiene standard through the trap assembly. For vinyl chloride calibration, 25 cc (effective concentration of 0.83 ppb) of 10 ppb standard is passed through the trap assembly. The trapped standards are then thermally desorbed into the chromatographic system for analysis. The calculated concentrations resulting from this analysis are compared to the "assigned" concentrations to insure consistency with previous calibrations. The stored data are then used to generate response factors used to calculate the concentrations of the analytes in subsequent samples. The instrument data system will not accept a response factor which differs from historic data by more than 15 percent. The response factor generated is tabulated in the instrument laboratory workbook. Attention must be given to trends in response factor values which may indicate instrument or detector sensitivity changes.

5) Multipoint calibrations are conducted every three months. Each multipoint calibration consists of a system blank and three standard concentration levels performed in triplicate. If data indicate that the analyses are consistently unacceptable, more frequent multipoint calibrations may be required.

6) Ambient samples are analyzed by drawing 300 cc (50 cc/minute, six minutes) through the Carbotrap preconcentrator, then desorbing the trapped hydrocarbons into the chromatograph as in the calibration step above. The resultant peaks are identified by retention times and quantitated relative to the calibration standards.

7.0 PERFORMANCE

a. Duplicate analyses are performed on 10 percent of all ambient samples received from the field. The relative percent difference of the duplicate analyses are recorded and included in the monthly Quality Control report. Only those data for concentrations in excess of the quantitation limits (0.40 ppb for 1,3-butadiene and 1.20 for vinyl chloride) are reported.

b. Cylinder AAL1728 (0.94 ppb 1,3-butadiene) is used as a control standard. The results of the daily control standard analyses are plotted on the Method Control Chart. If the result of any individual analysis falls outside the warning limits ($\pm 2\sigma$), the Control Standard shall be re-analyzed prior to the analysis of ambient samples. If subsequent data falls outside the method warning limits, or if an individual result falls outside the control limits ($\pm 3\sigma$), complete method validation must be performed. Method control chart for vinyl chloride shall be established as soon as a NBS traceable standard becomes available.

c. The FID which is connected in series to the PID will be used as a confirmation check for both compounds (see section 3.0 d).

8.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

The method sensitivity, precision and accuracy are outlined in Tables 2, 3, and 4. Multipoint analyses of a NBS traceable standard (AAL1728,0.94 ppb 1,3-butadiene) using both the PID and FID are presented in Tables 2A and 2B. Multipoint analyses of cylinder 62359 for vinyl chloride (10.0 ppb) using the same detectors are presented in Tables 3A and 3B.

Analyses of NBS traceable butadiene standards (AAL17249 and AAL1728) were carried out using our working standard, CC62053 for calibration and Nitrogen carrier gas as the sample matrix. Results are shown in Table 4. Analysis values for both standards are within 8% of their assigned values.

EPA audit cylinders (Groups IV and V) were also analysed using the NBS traceable standard, AAL17249 for calibration. Results as shown in Table 4 are within 4% of their assigned values.

Accuracy of the method for vinyl chloride will be determined upon availability of a NBS traceable standard.

Table 2A

METHOD SENSITIVITY AND PRECISION
FOR 1,3-BUTADIENE USING PID (Primary Detector)
(AAL1728, 0.94 ppb)

Sample Vol. (cc)	Estimated Conc., ppb	Mean Area Counts, n=3	Standard Deviation	RSD (%)
25	0.078	3027	243	8.0
50	0.156	6908	390	5.6
100	0.313	16776	934	5.6

Y-intercept = 1878
X-intercept = -0.032
Slope = 59134

Correlation Coefficient = 0.99851
Limit of Detection (LOD, ppb) = 0.040

Table 2B.

METHOD SENSITIVITY AND PRECISION
FOR 1,3-BUTADIENE USING FID (Confirmation Detector)
(AAL1728, 0.94 PPB)

Sample Vol. (cc)	Estimated Conc., ppb	Mean Area Counts, n=3	Standard Deviation	RSD (%)
150	0.47	202	28.6	14.2
300	0.94	593	95.7	16.1
600	1.88	1533	84.9	5.5

Y-intercept = -268
X-intercept = 0.28
Slope = 952

Correlation Coefficient = 0.99905
Limit of Detection (ppb) = 0.40

Table 3A

METHOD SENSITIVITY AND PRECISION
FOR VINYL CHLORIDE USING PID (Primary Detector)
(CC62359, 10 PPB)

Sample Vol. (cc)	Estimated Conc., ppb	Mean Area Counts, n=3	Standard Deviation	RSD (%)
25	0.833	14280	1450	10.2
50	1.67	29205	3182	10.9
100	3.34	61238	4464	7.2

Y-Intercept = -1699
X-Intercept = 0.090
Slope = 18795

Correlation Coefficient = 0.99984
LOD, ppb = 0.12

Table 3B

METHOD SENSITIVITY AND PRECISION
FOR VINYL CHLORIDE USING FID (Confirmation Detector)
(CC62359, 10.0 ppb)

Sample Vol. (cc)	Estimated Conc., ppb	Mean Area Counts, n=3	Standard Deviation	RSD (%)
25	0.833	897	200	22
50	1.67	2130	144	6.8
100	3.34	4284	164	3.8

Y-Intercept = -177
X-Intercept = 0.13
Slope = 1342

Correlation Coefficient = 0.99943
LOD, ppb = 0.22

Table 4

ANALYSIS OF NBS TRACEABLE STANDARDS FOR 1,3-BUTADIENE
(Based Upon Laboratory Working Standards Shown)

ANALYSED CYLINDER	CALIBRATION CYLINDER	ASSIGNED CONC.,ppb	AVERAGE CONC. FOUND,ppb	RSD (%)	BIAS (%)
17249	62053	1.85 +/-10%	1.85	3.1 (n=7)	0
1728	62053	0.94 +/-10%	0.87	2.9 (n=6)	-7.4
8184 (Grp.V)	17249	10.1	10.0	10.6 (n=11)	-1.0
16577 (Grp.IV)	17249	12.6	13.0	7.7 (n=3)	+3.2

Appendix C

Standard Operating Procedure for the Determination of 1,3-Butadiene in Motor Vehicle Exhaust

April 1990

Air Resources Board

PROCEDURE FOR THE ANALYSIS OF 1,3-BUTADIENE IN AUTOMOTIVE EXHAUST

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PROCEDURE FOR THE ANALYSIS OF 1,3-BUTADIENE IN AUTOMOTIVE EXHAUST

I. Introduction

1.1 This procedure describes a method of analyzing 1,3-butadiene in automotive exhaust in the range of 0.2 to 50 parts per billion concentrations by gas chromatography (GC) with photo-ionization detector (PID).

1.2 Lower concentrations may be analyzed by increasing the sample volume.

1.3 Higher concentrations may be analyzed by direct injection of a diluted sample or a smaller volume of sample through the cryogenic trap.

II. Method

2.1 A portion of the sample from a Tedlar bag is transferred by syringe to the heated volumetric sample loop or the cryogenic freeze-out trap of a gas chromatograph.

2.2 The sample is introduced into the chromatograph by means of a gas injection valve and analyzed by a photo-ionization detector.

2.3 The GC data system quantifies the 1,3-butadiene by integrating the peak area and calculating concentration from a factor determined during calibration with the 1,3-butadiene standard.

III. Apparatus

3.1 Tedlar bags, 2 mil thick, nominally of 0 to 100 liter capacity, and equipped with Quick-Connect fittings are used to contain the sample.

3.2 A gas chromatograph equipped with a gas injection valve,loop/freeze-trap inlet system, and a photo-ionization detector is used.

3.3 A stainless steel column (6' x 1/8 inch O.D.) packed with 0.19% picric acid on 80/100 mesh Carbopack-C coupled with a second column (6' x 1/8 inch O.D.) of N-octane on Porasil-C are used. These columns can be substituted by other columns which are capable of resolving 1,3-butadiene from other organic compounds with similar physical and retention properties.

3.4 An analog recorder and an electronic integrator are used to quantify peak areas.

3.5 Ground glass syringes (20, 50, 100, 250 ml) or other suitable devices are needed to transfer gas samples from Tedlar bags to the sample inlet of the gas chromatograph.

IV. Gases

4.1 All gases used to support the GC analysis shall be of the highest commercial purity available.

4.2 Helium shall have a minimum purity of 99.995%.

4.3 A Scott-Marin 1,3-butadiene cylinder is used as the control standard.

4.4 A NBS prepared 1,3-butadiene cylinder is used as the primary standard for daily calibration.

V. Procedure

5.1 The air sample is analyzed for 1,3-butadiene by using either the loop method or the cryogenic freeze-out method. The freeze-out method is used for measurement of low concentrations of 1,3-butadiene.

5.2 The procedure for the loop method follows:

5.2.1 The sample is transferred from the sample bag to sample inlet and injected into the sample loop of the gas chromatograph by means of a syringe fitted with Luer-Lok to a Quik-Connect adaptor.

5.2.2 The gas sampling valve is equipped with a 1 ml loop.

5.2.3 After the gas sampling valve is rotated, the sample enters the GC for analysis.

5.2.4 The 1,3-butadiene is separated from other organic compounds under the following GC operating conditions:

40 ml/min. helium carrier gas flow
50 deg C sample valve temperature
200 deg C detector temperature
50 deg C injector temperature
60 deg C isothermal column temperature

5.2.5 Concentrations of 1,3-butadiene are calculated by a Perkin Elmer LIMS system or similar system.

5.3 The procedure for the freeze-out method follows:

5.3.1 Immerse the sample trap in liquid nitrogen (LN_2) and allow the trap to cool down to liquid nitrogen temperature.

5.3.2 After discarding 50 ml of the sample, withdraw exactly 100 ml sample from the Tedlar bag with a 100 ml syringe and transfer the sample into the trap.

5.3.3 Back fill the syringe with another 20 ml of helium and flush the 20 ml through the trap; then flush helium through the trap for 3 minutes at 100 ml/min.

5.3.4 Rotate the valve to isolate the cryogenic trap and to allow the carrier gas to by-pass the trap.

5.3.5 Replace the liquid nitrogen Dewar with a Dewar containing hot boiling water (approx. 95 degrees C).

5.3.6 Allow the trap to warm up.

5.3.7 Rotate the valve and allow the carrier gas stream to flush the sample into the gas chromatograph.

5.3.8 The instrument operating conditions are the same as those described in Section 5.2.4 above.

VI. Calculations

6.1 The 1,3-butadiene concentration in ppb is calculated by the data system using the external standard method:

concentration = Area x Calibration Factor

6.2 The calibration factor (CF) is calculated during calibration by the equation

$$CF = \frac{\text{concentration}}{\text{area}}$$

The replicate calibrations are averaged and the arithmetic mean is stored as the CF to be used in subsequent analyses.

VII. Quality Control

7.1 Calibrations are performed daily with working and quality control standards. Accuracy of the method is determined with reference material.

7.1.1 A NBS reference material of 520 ppb and 6.4 ppb (parts per billion) 1,3-butadiene in nitrogen is used as the calibration standards.

7.1.2 A control standard is used daily to check the GC performance.

7.1.3 An assurance audit of the standards is performed quarterly.

7.2 Calibrations are performed on a daily schedule.

7.2.1 The daily calibration of GC performance consists of at least two for automotive exhaust analysis.

7.2.2 The calibrations are repeated on both quality control calibration standards if the response of the quality control check changes by more than 2 sigma standard deviation. If the calibrations fail on both standards, the GC system will be completely checked and a corrective action will be taken to bring the system under the control before any sample analysis.

7.2.3 If the lamp voltage is adjusted, allow time for the lamp to stabilize and repeat the calibrations.

7.2.4 A record is kept for the lamp voltage settings and all preventative maintenance procedures, i.e. lamp replacement, cleaning of lamp window.

7.2.5 Blank samples are run daily between calibrations and sample analyses as necessary.

7.3 Linearity is checked annually as time allows.

7.3.1 A gas chromatographic linearity check is performed with standards of at least four different concentrations. The concentrations must cover the anticipated range of sample concentrations.

7.3.2 Multipoint calibration

7.3.3 Any region of concentration that deviates more than 5% from the least square line is considered non-linear.

7.3.4 Samples are analyzed only in the linear range. (Figure 1).

7.4 Limits of detection are established.

7.4.1 The limit of detection (LOD) is calculated by the following equations:

(i) if $b>o$, $LOD = 3\ s/m$

(ii) if $b<o$, $LOD = \frac{|b|}{m} + \frac{3\ s}{m}$

LOD = 0.2 ppb

b,m = intercept, slope of calibration - curve near the LOD.

S = standard deviation of replicates.

7.4.2 The LOD should be determined at least on an annual basis.

7.4.3 If the calibration factor changes by more than 10%, the instrument must be checked and the LOD re-determined.

7.5 GC column condition parameters should be checked and documented.

7.5.1 All GC parameters should be checked daily and recorded.

7.5.2 The efficiency and resolution of the column should be checked frequently. If there is more than 10% change, the column needs replacement.

7.5.3 If the headpressure required to maintain a specified flow through the column increases by more than 100%, the column needs replacement.

7.5.4 If the drift of retention times of the peaks results in peak misidentification, all instrument parameters need to be checked.

7.6 Replicate analyses are performed daily.

7.6.1 A duplicate analysis is performed on at least one ambient sample. A duplicate analysis is not performed with exhaust samples due to the high reactivity and decay of 1,3-butadiene.

7.6.2 If the duplicate analysis differs by more than 20% and if the concentration of the sample is higher than 3 x LOD, then an additional analysis is needed.

7.6.3 If the relative standard deviation (RSD) of the replicate analyses is greater than 15% and if the concentration of the sample is greater than 3 x LOD, none of the analyses for that day are acceptable.

7.6.4 If the range is within 20%, the mean and the standard deviation are reported.

7.7 Compound confirmation is required in quality control procedures.

7.7.1 At least 10% of the analyses are to be confirmed by a different analytical system. e.g. different columns or detector (GC/MS).

VIII. Critique and Comments

8.1 The minimum measurable concentration of 1,3-butadiene has been determined to be 0.2. ppb using this method with 100 ml freeze-out.

8.2 Any organic compound present in the sample having a retention time similar to that of 1,3-butadiene under operating conditions described in this method may interfere with the quantification.

8.3 Proof of chemical identity for 1,3-butadiene requires confirmation by other means.

8.4 1,3-butadiene can be positively identified by a gas chromatograph/mass spectrometer.

8.5 This method has been proven to be useful in analyzing ambient air or vehicle emission exhaust samples.

8.6 Exhaust samples must be analyzed as soon as received because 1,3-butadiene is extremely reactive and decays in the Tedlar bag. Most of the 1,3-butadiene is in Mode 1 of the dyno CVS sample. That sample is to be run within 5 minutes after received. The time when the sample is analyzed must be recorded.

Appendix D

Glossary

GLOSSARY

Actinic Region: The region of the radiation spectrum that can cause photochemical activity.

Adiponitrile: A chemical intermediate used in the manufacture of nylon.

Alkene: A class of unsaturated aliphatic hydrocarbons having one or more double bonds obtained by thermal cracking of petroleum fractions at high temperature (e.g., 1,3-butadiene).

Arrhenius Equation: A mathematical equation used to determine the rate of a chemical reaction with rise in temperature.

Biradical: Paired radicals, as in the case of the $\left[\dot{C}H_2O\dot{O}\right]^{\ddagger}$ radical.

Copolymer: An elastomer produced by the simultaneous polymerization of two or more dissimilar monomers (e.g., rubber from styrene and butadiene).

Criegee Reaction: Cleavage (division) of a compound into two compounds.

Dialkene: An unsaturated aliphatic hydrocarbon having two double bonds (e.g., 1,3-butadiene).

Elastomer: Synthetic polymers having properties similar to those of natural rubber, namely, the ability to be stretched to at least twice their original length and retract very rapidly to (approximately) their original length upon release.

Emission Factor: The rate of emission of a particular substance from an emission source.

Limit of Detection (LOD): The quantifiable limit (threshold) at and above which a substance can be accurately and precisely given a concentration value.

Monomer: A simple molecule or compound usually containing carbon and capable of conversion to polymers, elastomers, or synthetic resins by combination with itself or other similar molecules or compounds (e.g., styrene, the monomer from which polystyrene resins are produced).

Oxidative Dehydrogenation: The process whereby hydrogen is removed from compounds by chemical means, considered a form of oxidation.

Partially Observed Data (POD): An expression used to indicate (for a series of environmental measurements) that at least one of the measurements was found to be below the detection limit of the measurement method.

Pharmacokinetic Data: Data derived from a model that considers multiple routes of exposure to a substance (total body burden) and the substance's metabolism/deposition/excretion to and from various organs in an organism's body.

Polymer: A macromolecule formed by the chemical union of five or more identical combining units called monomers.

Population-weighted Exposure Estimate: An estimate of exposure to a substance that adds more weight (emphasis) to a site that represents a large population than it does to a site representing a smaller population.

Radical: A highly reactive substance having a charge (either positive or negative), that can act as an initiator or intermediate in combustion, oxidation, or polymerization.

Troposphere: The portion of the atmosphere (extending from ground level to around six kilometers above the ground) where weather occurs and pollutants are concentrated.

Unsaturated Aliphatic Hydrocarbon: An open-chain compound containing only carbon and hydrogen, capable of forming addition products because of its unsatisfied valence state (e.g., 1,3-butadiene).