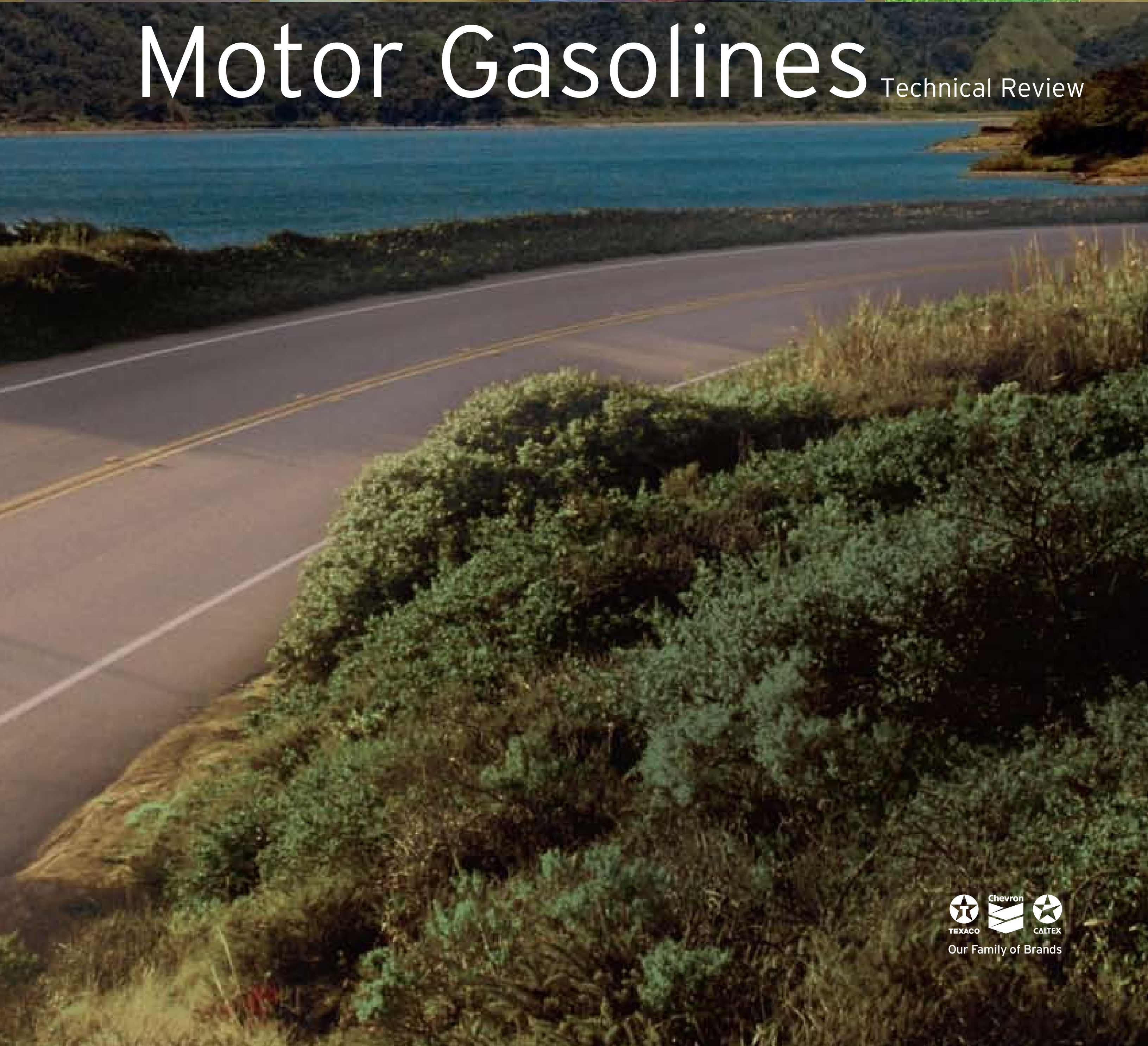
Chevron

Motor Gasolines
Technical Review



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Introduction

In May 1876, Nicolaus Otto built the first practical four-stroke-cycle internal combustion engine powered by a liquid fuel. By 1884, he concluded development of his engine with the invention of the first magneto ignition system for low-voltage ignition. The liquid fuel used by Otto became known as gasoline in the United States; elsewhere it may be known as *gasolina*, *petrol*, *essence*, or *benzin* (not to be confused with the chemical compound benzene).

Although the U.S. petroleum industry was almost 50 years old when the first Model T rolled off Henry Ford's production line in 1908, gasoline and the automobile grew up together. The industry was born in August 1859 near Titusville, Pa., when a drilling effort financed by Edwin Drake hit crude oil at a depth of 70 feet (21 meters). The major product in the early years wasn't gasoline; it was lamp oil, called *coal oil* or *kerosene*.[1] People were reading more and wanted better light than that provided by candles and whale oil lamps. The natural gasoline in crude oil was a surplus byproduct. Being too volatile to use in lamps, it was burned at refineries, dumped, or converted to a gaseous fuel for gas lights.

The development of the electric light and the astonishing popularity of the automobile in the first decades of the 20th century turned the petroleum industry's focus from kerosene to gasoline. In 1911, gasoline sales exceeded kerosene sales for the first time. The simple engines in the first cars ran on almost any liquid that burned. As the demand for power increased and engines became more sophisticated, gasoline was recognized as the right fuel for the spark-ignition internal combustion engine.[2]

Drivers can obtain the performance they expect only when the characteristics of the fuel they use match the fuel requirements of the engines in their cars. As a result of this correlation, the gasoline engine and its fuel matured as mutually dependent partners. An engine was not designed without considering the gasolines available in the marketplace. In turn, gasoline was not made without considering the requirements of the engines that would burn it. The partnership became a triumvirate in the last decades of the 20th century as environmental considerations began to change both engine design and gasoline characteristics.

This review collects information about all three members of the triumvirate in one place. The major focus is gasoline – its performance, characteristics, refining and testing, and safe use. Significant space is also devoted to the operation of modern engines and to the impact of environmental regulations on both engines and fuels. Numerous cross-references emphasize how interconnected these topics are. We hope readers will find the review a source of valuable information, whether they read it from cover to cover or focus on an area of interest.

Please note: The information in this review may be superseded by new regulations or advances in fuel or engine technology.

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[1] Both the names *coal oil* and *kerosene* were holdovers from the previous decades when lamp oil was distilled from coal. Kerosene, a corruption of the Greek words for wax and oil, was one American company's brand name for coal oil.

[2] Petroleum Panorama, *The Oil and Gas Journal*, 57 (5), January 28, 1959.

2 • Gasoline and Air Quality

Today, we commonly discuss gasoline or gasoline-powered vehicles and their impact on air quality. A number of metropolitan areas in the U.S. fail to meet one or more federal air quality standards. In some of these areas, on-road vehicles are responsible for more than half of the emissions that either primarily or secondarily cause violations of air quality standards. Other major metropolitan areas throughout the world also are experiencing serious air pollution problems.

This chapter explains who regulates emissions and how and why they do it. It also explains which emissions come from vehicles and how those emissions are formed. Finally, it explains how emissions are affected by gasoline characteristics and how gasoline is being reformulated to help reduce emissions.

The explanations are complicated because they involve complex regulations and complex science. As a consequence, keeping this review short and simple is challenging. The numerous acronyms and abbreviations are unavoidable; both government regulation and science use them heavily.

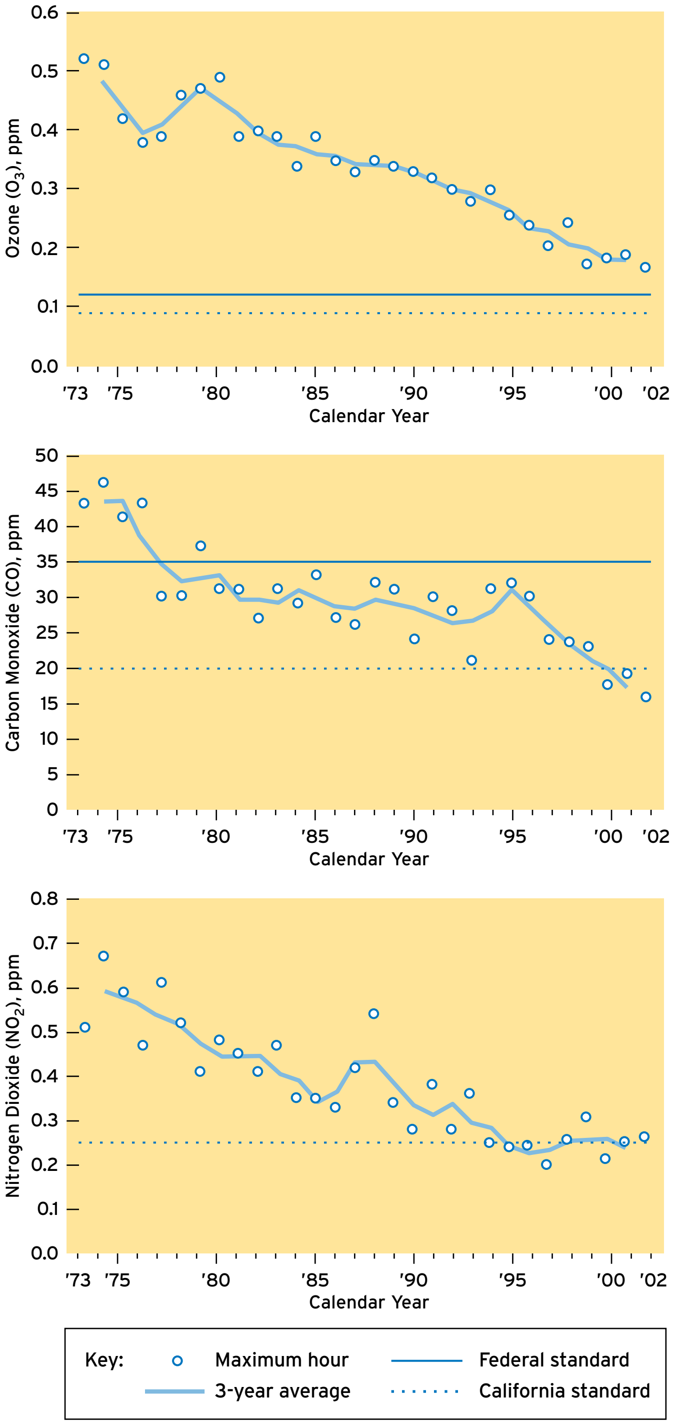
PROGRESS IN THE UNITED STATES

Are the efforts of adding pollution control systems to vehicles and reformulating gasoline paying off in better air quality? The answer is yes. Urban air quality has improved dramatically over the past 30 years. To illustrate, Figure 2.1 shows the declining trends for the maximum hourly concentrations of three air pollutants, ozone (O_3), carbon monoxide (CO), and nitrogen dioxide (NO_2), in California. Decreases are not uniform from year to year because of the effect of weather variations on ambient pollutant concentrations.

Improved urban air quality is the result of significant reductions in emissions from various emission source categories such as factories, power plants, consumer products, and automobiles. For example, today a new-model passenger car emits less than 1 percent of the volatile organic compounds (VOCs), less than 5 percent of the carbon monoxide, and only about 7 percent of the oxides of nitrogen (NO_X) emitted by a vehicle built before emission controls were implemented. Similarly impressive improvements have been achieved in other emission source categories.

Figure 2.1

Maximum Hourly Pollutant Levels in California 1973-2002



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The Beginning

Smog is the common term for the forms of air pollution involving haze and oxidants, such as ozone. Smog was identified as a serious problem in the Los Angeles basin in the 1950s. As university scientists and government health agencies investigated the problem, they found that vehicle emissions were a significant source of smog precursors. Acting on this information, the California legislature established emissions limits for 1966-model cars. Federal legislation to reduce vehicular emissions, as part of a greater air quality program, was initiated with the adoption of the Clean Air Act of 1963. The first federal limits for exhaust emissions from gasoline-powered cars were implemented starting with the 1968 model year.

The introduction of reformulated gasolines (RFG) also has helped improve air quality. Federal Phase I RFG was introduced in January 1995, Phase II in January 2000. California Phase 2 RFG was required in California in mid-1996, and Phase 3 was required at the end of 2003. Federal Phase II and California Phase 2 and Phase 3 reformulated gasolines are believed to reduce ozone-forming emissions from cars and light trucks by 10 percent to 15 percent. This effect is not apparent in Figure 2.1 because of the year-to-year variability caused by factors such as weather.

LEGISLATION

In the United States, federal legislation regarding air pollution began with the Air Pollution Control Act of 1955. Air pollution *control* legislation was initiated with the Clean Air Act of 1963 and expanded under the Air Quality Act of 1967 and the Clean Air Act of 1970. The 1970 act was amended in 1977 and most recently in 1990.[1] Designed to manage the nation's air quality and to advance regional air pollution prevention and control programs, the act is wide-ranging, addressing a variety of air pollution issues. However, in the area of vehicle emissions, it is restrictive, forbidding states from setting separate vehicle emissions standards. This restriction was included so that auto manufacturers would not have to produce cars with different emission control systems to meet different state standards. The restriction was waived for California. With its more severe smog levels and its long history of working to control vehicle emissions, California is allowed to establish its own regulations for controlling vehicle emissions, subject to federal approval. Under certain circumstances, other states are allowed to require the sale of new vehicles that meet the more stringent California standards.

ADMINISTRATION/REGULATION

Laws are not administered by the body that adopts them. The U.S. Congress or state legislature assigns the administrative responsibility to a governmental agency. In 1970, the National Environmental Policy Act created the U.S. Environmental Protection Agency (EPA) and made it responsible for implementing the requirements of the federal Clean Air Act and its amendments. California's laws covering vehicle emissions are administered by the California Air Resources Board (CARB), which was established by the state legislature in 1967.

While some laws contain a lot of detail, they can't address all the issues surrounding their application in our complex industrial society. The agency administering the law has the responsibility to write regulations that will make the legislative intent a reality. Title 40 of the Code of Federal Regulations (CFR) contains U.S. EPA regulations concerning the protection of the environment.

The states, as Congress intended, do much of the work to carry out the provisions of the federal Clean Air Act and its amendments. State and local air pollution agencies hold hearings, write regulations (based on guidance from the U.S. EPA), issue permits, monitor

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[1] "History of the Clean Air Act," U.S. EPA, *http://epa.gov/air/caa/caa_history.html.*

pollution, issue notices of violations, and levy fines. It is appropriate for the states to take the lead because state and local agencies need to select and enforce pollution control strategies that make sense for their region. Geography, weather conditions, housing patterns, regional traffic patterns, and the nature of local industry all influence pollution levels.[2]

The Clean Air Act and its amendments specify deadlines for the U.S. EPA, states, local governments, and businesses to reduce air pollution. Each state is required to develop a plan that explains the actions it will take to meet or maintain the air quality standards set by the U.S. EPA. A *state implementation plan* (*SIP*) is a collection of the regulations a state will use. The U.S. EPA must approve each state's SIP. The U.S. EPA assists the states by providing scientific research, expert studies, engineering designs, and money to support clean-air programs.

AIR QUALITY STANDARDS

Air pollutants are natural and artificial airborne substances that may be introduced into the environment in a sufficient concentration to have a measurable effect on humans, animals, vegetation, or building materials. From a regulatory standpoint, substances become air pollutants when the U.S. EPA determines them to be. As part of the process, the Clean Air Act requires the U.S. EPA to issue a *criteria document* that provides details on the adverse effects of individual pollutants. Regulated pollutants therefore are referred to as *criteria pollutants*. The U.S. EPA uses the information in the criteria documents to set National Ambient Air Quality Standards (NAAQS) at levels that protect the public health and welfare. Table 2.1 lists criteria pollutants and their federal limits. California standards, which in most cases are more stringent, also are listed. Some of the criteria pollutants, such as carbon monoxide, are *primary pollutants*, which are emitted directly by identifiable sources. Others, such as ozone, are *secondary*

Table 2.1

U.S. Ambient Air Quality Standards

Criteria Pollutant	Averaging Time	Maximum Average Concentration	
		Federal Standard	California Standard
Ozone, ppm	1-hour 8-hour	– 0.075	0.09 0.070
Carbon monoxide (CO), ppm	1-hour 8-hour	35 9	20 9.0
Nitrogen dioxide (NO_2), ppm	1-hour Annual	– 0.053	0.18 0.030
Sulfur dioxide (SO_2), ppm	1-hour 24-hour Annual	– 0.14 0.030	0.25 0.04 –
Suspended particulate matter (PM_{10}), µg/m^3	24-hour Annual	150 –	50 20
Suspended particulate matter ($PM_{2.5}$), µg/m^3	24-hour Annual	35 15	– 12
Lead, µg/m^3	30-day Quarterly	– 1.5	1.5 –
Sulfates, µg/m^3	24-hour	–	25
Hydrogen sulfide, ppm	1-hour	–	0.03
Vinyl chloride, ppm	24-hour	–	0.01

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[2] *The Plain English Guide to the Clean Air Act*, EPA-456-07-001, April 2007. Available online at *http://www.epa.gov/air/caa/peg/*.

Table 2.2

European Union Ambient Air Quality Standards
(Directives 1999/30/EC, 2000/69/EC, 2002/3/EC, 2004/107/EC)

Pollutant	Legal Nature*	Concentration, max	Averaging Period	Effective Date	Permitted Exceedences Each Years
Sulfur dioxide (SO_2), µg/m^3	Limit	350 125 20	1-hour 24-hour Annual and winter**	Jan. 1, 2005 Jan. 1, 2005 July 19, 2001	24 3 –
Nitrogen dioxide (NO_2), µg/m^3	Limit	200 40	1-hour Annual	Jan. 1, 2010 Jan. 1, 2010	18 –
Nitrogen oxides (NO_X), µg/m^3	Limit	30	Annual	July 19, 2001	–
Suspended particulate matter (PM_{10}), µg/m^3	Limit	50 40	24-hour Annual	Jan. 1, 2005 Jan. 1, 2005	35 –
		50 20	24-hour Annual	Jan. 1, 2010 Jan. 1, 2010	7 –
Lead (Pb), µg/m^3	Limit	0.5	Annual	Jan. 1, 2005	–
Carbon monoxide (CO), µg/m^3	Limit	10	Maximum daily 8-hr mean	Jan. 1, 2005	–
Benzene, µg/m^3	Limit	5	Annual	Jan. 1, 2010	–
Ozone, µg/m^3	Target	120	Maximum daily 8-hr mean	Jan. 1, 2010	25 days averaged over 3 years
Arsenic (As), ng/m^3	Target	6	Annual	Dec. 31, 2012	–
Cadmium (Cd), ng/m^3	Target	5	Annual	Dec. 31, 2012	–
Nickel (Ni), µg/m^3	Target	20	Annual	Dec. 31, 2012	–
PAH as Benzo(a)pyrene, ng/m^3	Target	1	Annual	Dec. 31, 2012	–

*Limit value is legally binding; target value is to be attained as far as possible by the attainment date and is less strict than a limit value.
**Limit applies for calendar year as well as the Winter Period (Oct. 1 to March 31).

pollutants, which are formed by reactions in the atmosphere. Still others, such as particulates, are of mixed origin. Table 2.2 shows the ambient air quality standards for the European Union (EU).

AIR POLLUTANTS

Ozone (O_3) Ground-level ozone[3] is a colorless gas that is the chief component of urban smog. It is formed by the interaction of reactive organic gases, NO_X, and sunlight. These reactions take time, which means that peak ozone concentrations can occur far downwind of reactant sources. Weather plays an important role; high temperatures, stagnant air, and sunny skies are optimum for creating ozone. This is why ozone concentrations tend to be highest in the summer months and are higher in the afternoon than at night.

Early in their regulatory histories and for decades thereafter, the U.S. EPA and the state of California used one-hour standards for ground-level ozone to identify nonattainment areas.

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[3] In the stratosphere, a layer of ozone partially shields the earth from solar ultraviolet radiation. Stratospheric ozone is formed by a mechanism that is different from that which forms ground-level ozone.

(One-hour refers to the time frame in which ozone concentrations are averaged on a daily basis; the broader the time frame, the more likely an area is to exceed a standard's threshold.) In 1997, the U.S. EPA promulgated a new eight-hour standard believed to be more protective of human health. It also specified a threshold of 0.08 parts per million (ppm). Litigation delayed implementation of the new standard until April 2004. In 2008, the U.S. EPA revised its ground-level ozone standard to 0.075 ppm, extending the measurement to the third decimal place (see Table 2.1). While maintaining a one-hour standard, California adopted an additional eight-hour ground-level ozone standard in 2005.

Ozone levels have decreased 20 percent, on average, nationwide since 1980.[4]

Exposure to ozone has been linked to a number of health effects, including significant decreases in lung function, inflammation of the airways, and increased respiratory symptoms. Ozone also affects vegetation and ecosystems, leading to reductions in agricultural crop and commercial forest yields. In the U.S., ground-level ozone is responsible for an estimated $500 million in reduced crop production each year.[5]

Volatile Organic Compounds (VOCs)[6] VOCs are not criteria pollutants, although some specific VOCs are classified as toxics (see later sections). The importance of VOCs stems from their role in forming ozone. Most hydrocarbon (HC) emissions are VOCs, which explains why so much effort is directed toward reducing HC emissions from vehicles and other source categories.

Global VOC emissions primarily come from vegetation (377 million metric tons carbon equivalent annually), fossil fuels (161 million metric tons carbon equivalent annually), and biomass burning (33 million metric tons carbon equivalent annually).[7] In the 20-year period from 1983 to 2002, anthropogenic VOC emissions in the U.S. decreased by 40 percent.[8] On-road gasoline vehicles accounted for about 26 percent of man-made VOC emissions in 2002 (Figure 2.2), the last year for which U.S. EPA data are available.

Not all hydrocarbons contribute equally to ozone formation. Some are more reactive than others, depending on their chemical structure and the atmospheric conditions to which they are subjected. Under most conditions, olefins and aromatics are more reactive than paraffins.

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[4] "Air Trends, Ozone," U.S. EPA, *http://www.epa.gov/airtrends/ozone.html*.

[5] "Ozone – Good Up High Bad Nearby," U.S. EPA, *http://epa.gov/oar/oaqps/gooduphigh/*.

[6] VOC is the preferred term when discussing emissions. When the focus is on ozone formation, the term *reactive organic gases* (*ROGs*) is more common. The main difference is that VOC emissions include methane and ethane, which do not participate in ozone formation and thus are not ROGs. Another term sometimes used is *non-methane organic gases* (*NMOGs*). For simplicity, this review will use the term VOC throughout.

[7] "Emissions of Greenhouse Gases in the United States 2003," Energy Information Administration, Department of Energy, *ftp://ftp.eia.doe.gov/pub/oiaf/1605/cdrom/pdf/ggrpt/057303.pdf*.

[8] "National Air Quality and Emissions Trends Report, 2003 Special Studies Edition," Air Quality Trends Analysis Group, U.S. EPA, Research Triangle Park, N.C., September 2003. Available online at *http://www.epa.gov/airtrends/aqtrnd03/*.

Figure 2.2

Emissions Sources:
2002 National Man-Made VOC Emissions
16,544,000 short tons

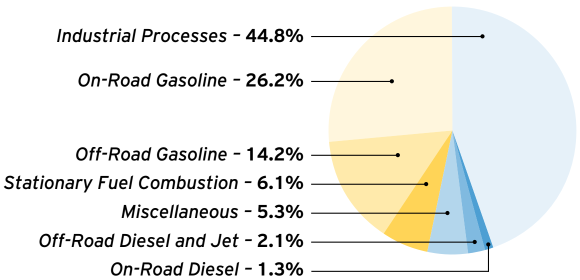


Figure 2.3

Emissions Sources:
2002 National Man-Made Carbon Monoxide Emissions
112,049,000 short tons

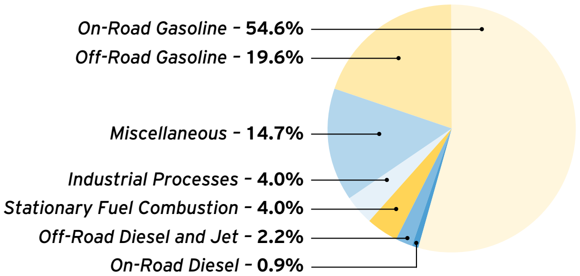
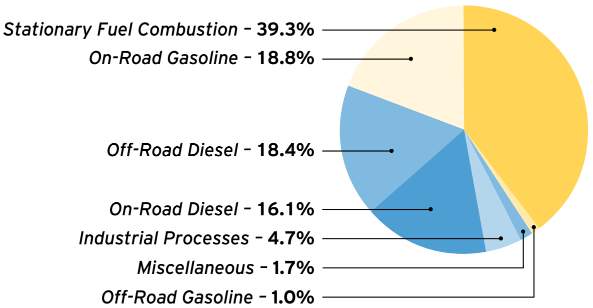


Figure 2.4

Emissions Sources:
2002 National Man-Made Nitrogen Oxide Emissions
21,102,000 short tons



Source: U.S. EPA, "Air Trends September 2003 Report: National Air Quality and Emissions Trends Report, 2003 Special Studies Edition."

Carbon Monoxide (CO) CO is a colorless, odorless gas generated primarily by combustion processes. It is toxic to humans and animals, and at high enough levels, CO causes headaches, nausea, and even death. CO toxicity stems from its ability to reduce the oxygen-carrying capacity of the blood by preferentially bonding to hemoglobin.

CO is formed when carbon in fuel is not burned completely. The highest ambient levels generally occur during the colder months, when atmospheric temperature inversions are more common, trapping CO emissions near the surface of the earth under a layer of warmer air. The U.S. EPA estimated that on-road gasoline vehicles were responsible for about 55 percent of man-made CO emissions nationwide in 2002 (Figure 2.3). In major cities, however, 85 percent to 95 percent of all CO emissions come from motor vehicle exhaust. Over the last decade, the auto industry has made remarkable advances in tightly controlling air-fuel ratio (A/F), which reduces CO emissions. This, combined with continuing refinements in catalyst technology that cleans up pollutants from engine exhaust, has helped to drastically reduce CO emissions from today's cars.

Nitrogen Oxides (NO_X) NO_X is the generic term for several reactive gases containing nitrogen and oxygen in various ratios. They form when fuel is burned at high temperatures. The U.S. air quality standard applies only to nitrogen dioxide (NO_2), but where emissions are concerned, NO and NO_2 are usually analyzed simultaneously and expressed as NO_X. This is because NO oxidizes in the atmosphere to form NO_2, a more toxic compound. Most NO_X emissions (90 percent) are man-made. The main sources are motor vehicles and industrial/commercial sources that burn fuels. The U.S. EPA estimated that on-road gasoline vehicles generated about 19 percent of man-made NO_X emissions in 2002 (Figure 2.4).

NO is nontoxic by itself, but it contributes to ozone formation. The resulting atmospheric product, NO_2, can irritate lungs and lower resistance to respiratory infection. In some western areas of the United States, NO_X is an important precursor to particulate concentrations.[9]

Sulfur Dioxide (SO_2) SO_2 is produced primarily from the combustion of fuels containing sulfur. Facilities that burn fuel oil and coal are the major sources. On-road and off-road engine fuels are estimated

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[9] "National Air Quality and Emissions Trends Report, 2003 Special Studies Edition," Air Quality Trends Analysis Group, U.S. EPA, Research Triangle Park, N.C., September 2003. Available online at *http://www.epa.gov/airtrends/aqtrnd03/*.

to be the source of less than 3 percent of total SO_2 emissions, and this contribution further declined because of the implementation of the U.S. EPA's ultra-low sulfur diesel fuel regulations and similar sulfur limits in Europe and many other countries.

SO_2 is a moderate lung irritant. Both SO_2 and NO_X are major precursors to acidic deposition (acid rain).

Particulate Matter (PM_{10} and $PM_{2.5}$) PM_{10} is composed of airborne particles less than 10 microns (0.0004 inch) in diameter. (For comparison, the diameter of a human hair is 50 microns to 100 microns). The U.S. EPA estimates that fugitive dust from roads accounts for about two-thirds of total PM_{10} emissions. Less than 2 percent is attributed to on-road and off-road engines, but the percentage is higher in urban areas. PM_{10} attributable to vehicle exhaust includes both primary carbon particles (mainly from diesel) and secondary sulfate and nitrate aerosols formed by reactions of SO_2 and NO_X in the atmosphere. Both the U.S. EPA and California have established PM_{10} standards.

$PM_{2.5}$ is a subset of PM_{10} composed of particles less than 2.5 microns in diameter. Such particles are small enough to reach deep in the lungs and may contain substances particularly harmful to human health. The U.S. EPA promulgated national 24-hour and annual $PM_{2.5}$ standards in 1997. In 1999, the U.S. EPA and its state, tribal, and local air pollution control partners deployed a monitoring network to measure $PM_{2.5}$ concentrations nationwide and have accumulated data for several years. The U.S. EPA used these data to identify geographic areas not attaining the standards and issued notices of nonattainment in 2005, which started the clock on establishment of SIPs for affected areas.

Lead Gasoline-fueled vehicles were the primary source of airborne lead when gasoline contained a lead alkyl antiknock additive, such as tetraethyl lead (TEL). In the U.S. between 1970 and 1994, the lead content in leaded gasoline was phased down, sales of unleaded gasoline increased, and total national lead emissions decreased sharply. The sale of gasoline containing lead additives was finally prohibited for on-road use in January 1996. On-road gasoline-fueled vehicles in the U.S. today are not responsible for atmospheric lead concentrations.

Excessive exposure to lead may cause neurological impairments such as seizures, mental retardation, and behavioral disorders. Fetuses, infants, and children are especially vulnerable even to low doses of lead. The hazardous threshold for blood lead poisoning is still being disputed.

Toxic Organics The toxicity of organic compounds depends on their structure. Most hydrocarbons are nontoxic at low concentrations, with benzene a notable exception. Some low-molecular-weight aldehydes are carcinogens, and some monocyclic and polycyclic aromatic hydrocarbons (PAH)[10] are suspected or known carcinogens.

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[10] Also called polycyclic organic matter (POM); consists of polycyclic aromatic hydrocarbons (PAH), including benzo(a)pyrene, their nitrogen analogs, and a small number of oxygen-containing polycyclic organic matter compounds.

Fuel Economy and Emissions

Intuition suggests that one engine that burns more fuel than another over a given distance would produce more emissions, but that is not true. Vehicle emissions standards for new vehicles are set in terms of the mass of pollutant emitted per distance traveled. So, for example, a heavy, large-engine passenger vehicle may burn twice as much fuel as a lighter, small-engine vehicle over a given distance, but both vehicles must meet the same emissions standards and both will produce equivalent emissions per distance traveled. The large-engine vehicle in this example will, however, produce twice as much CO_2 *as the small-engine vehicle.* CO_2 *is the result of complete oxidation of the carbon atoms in gasoline, and the amount of* CO_2 *produced is directly proportional to fuel economy. Pursuant to a Supreme Court ruling in 2009, the U.S. EPA issued a proposed finding that greenhouse gases, including* CO_2*, contribute to air pollution that may endanger public health or welfare. The U.S. Congress and the U.S. EPA are pursing legislation and regulation that will reduce greenhouse gases, including limits on fuels and vehicle economy. In Europe, the auto industry has a target of 140g* CO_2*/km for the new-car fleet by 2008. Europe uses g* CO_2*/km as a more appropriate fuel economy measure because the fleet includes both gasoline- and diesel-fueled passenger cars.*

The Clean Air Act Amendments of 1990 classified the following as toxic air pollutants related to gasoline and gasoline vehicles:

- Benzene
- Polycyclic organic matter (POM)
- Acetaldehyde
- Formaldehyde
- 1,3-Butadiene

The U.S. EPA calculates that these five toxic compounds comprise 3.8 percent of total VOC emissions. About 70 percent of that amount is benzene. 1,3-Butadiene, formaldehyde, and acetaldehyde are not present in gasoline; they are formed during combustion.

Benzene is a known human carcinogen. Some POMs are also carcinogens, but the POM content of gasoline and gasoline exhaust is so low as to be difficult to measure. The two aldehydes are eye and throat irritants, and formaldehyde is a suspected human carcinogen.

ORIGIN OF VEHICLE EMISSIONS[11]

When fuel is burned with the correct amount of air in a gasoline-powered engine, the gases that are left are predominantly water vapor, carbon dioxide, and nitrogen. All of these gases are benign, although carbon dioxide is a greenhouse gas. Deviations from ideal combustion lead to the production of some VOCs, CO, NO_X, and PM_{10}.[12]

As noted earlier, gasoline-powered vehicles tend to be the main source of CO emissions, and they contribute substantially to urban VOC and NO_X emissions. However, significant improvement in emission controls on new cars has diminished their contribution of these pollutants. New cars emit only modest amounts of PM_{10} and $PM_{2.5}$, but vehicles that are ill-maintained or tampered with can emit much more. Older diesel-powered vehicles without particulate traps, on the other hand, are substantial emitters of PM_{10}, $PM_{2.5}$, and NO_X but only small emitters of CO and VOCs. (See figures 2.2, 2.3, and 2.4.)

Exhaust VOC The vast majority of gasoline is burned before combustion gases exit the engine in a properly operating vehicle, but a small fraction, typically 1 percent to 5 percent, escapes the combustion chamber unburned. These VOC emissions consist primarily of unburned hydrocarbons, but partially burned oxygen-containing compounds such as aldehydes are also present in small amounts. Most are removed by a vehicle's catalytic converter. The quantity of exhaust VOC emissions is influenced by many factors, including engine design, controls, and condition; operating temperature; A/F; fuel system deposits; and catalytic converter performance. If a vehicle has a malfunctioning component that inhibits proper ignition or combustion, such as a bad spark plug, VOC emissions can be many times higher than normal.

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[11] A significant amount of emissions-related information may be obtained from the U.S. EPA Office of Transportation and Air Quality site at *http://www.epa.gov/otaq/index.htm.*

[12] For details on pollutant formation and control in gasoline engines, see John B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988.

Evaporative VOC Exhaust gases are not the only source of VOC emissions from gasoline-fueled vehicles. In fact, the U.S. EPA estimated that in 1990 more than half the VOCs emitted from gasoline vehicles came from evaporation. Evaporative VOC emissions differ from exhaust VOC emissions in that evaporative emissions contain no combustion products. Because evaporative VOC emissions originate largely from gasoline vapor, their composition is weighted heavily toward the lowest boiling components of gasoline.

Gasoline vapor escapes from a typical vehicle at various points, including the fuel tank, carburetor (on vehicles that use them), and intake manifold. In addition, liquid gasoline can permeate plastic fuel tanks and elastomeric fuel hoses, and the permeation effects are greater with ethanol-blended gasoline. Liquid gasoline can also leak or seep from fuel system components or connections.[13] Factors that influence the amount of evaporative emissions include:

- Fuel system design (see page 65)
- Component integrity
- Ambient temperature
- Gasoline vapor pressure (see page 2)
- Gasoline composition

Of course, a certain amount of gasoline vapor is lost during fueling, though most of it may be collected by service station vapor recovery systems, where installed.

Carbon Monoxide CO is the result of incomplete combustion of fuel, and the main factor influencing its production is the ratio of air to fuel in an engine combustion chamber. If the mixture of air and gasoline is fuel-rich, that is, has insufficient air (O_2) to convert all fuel carbon to carbon dioxide (CO_2), the exhaust will contain a high level of CO. Fuel-rich operation can result either by design or by accident.

Prior to the introduction of vehicle emissions standards, most gasoline vehicles ran slightly fuel-rich most of the time and produced a lot of CO. Later, manufacturers designed vehicles to minimize fuel enrichment but also to allow for short periods of enrichment to aid vehicle starting and to increase power output under certain conditions. Today's cleanest vehicles use minimal or no cold-start enrichment. Power enrichment is being greatly reduced since the U.S. EPA bolstered its vehicle certification requirements with the Supplemental Federal Test Procedure (SFTP), which tests for emissions at high-speed and under high-power conditions.

Irrespective of its design, a vehicle may operate fuel-rich when its fuel supply or control system accidentally malfunctions. The causes are many but include:

- Deterioration or failure of components such as the carburetor or oxygen sensor.
- Deposits formed over time in fuel injectors or carburetors by poor-quality gasoline.
- Maintenance deficiencies such as maladjustment or neglect.

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[13] In these cases, the composition of the evaporative VOCs will be characteristic of the whole gasoline.

Oxides of Nitrogen NO_X is produced differently than CO and exhaust VOCs. The latter are products of incomplete combustion; NO_X is produced when combustion is robust. It is generated by reactions of nitrogen and oxygen, which occur at high temperatures. Nitrogen is always present in a combustion chamber because air is roughly 80 percent nitrogen. The production of NO_X occurs whenever residual oxygen is present during combustion and is particularly prevalent with higher combustion temperatures. Thus, NO_X is affected by the A/F and by engine design factors that influence temperature, such as compression ratio, spark timing, and cooling system performance. Combustion chamber deposits are believed to have a modest insulating effect that raises combustion temperatures and increases NO_X emissions slightly.

VEHICLE EMISSIONS: LIMITS

The Clean Air Act required the U.S. EPA to set standards or limits for exhaust emissions from gasoline-powered cars starting with the 1968 model year. These first limits applied to CO and hydrocarbons, with limits for NO_X added starting in the 1973 model year. Table 2.3 shows how U.S. limits for passenger cars, expressed as grams per mile (g/mile), have been tightened over the years. Beginning in 1994, vehicles were certified for longer life spans and the emissions limits for the first five years/50,000 miles became more stringent, as shown in Table 2.3. Beginning in 2004 with full implementation in 2007 for light-duty vehicles, the new federal Tier 2 120,000-mile tailpipe standards established eight permanent and three temporary "certification bins" with an average standard of 0.07 g/per mile for NO_X for all classes of passenger vehicles, sport utility vehicles, and light-duty trucks.

Table 2.3

U.S. Federal Passenger Car Exhaust Emission Standards

Model Year	Useful Life, Years/1M Miles	Maximum Emissions g/mile (FTP-75 Cycle)			
		Carbon Monoxide (CO)	Hydrocarbons (HC)	Oxides of Nitrogen (NO_X)	Particulates (PM_{10})
Pre-control (estimated)	–	84	10.6	4.1	–
1968-69	5/50	51	6.3	–	–
1970-71	5/50	34	4.1	–	–
1972	5/50	28	3.0	–	–
1973-74	5/50	28	3.0	3.1	–
1975-76	5/50	15	1.5	3.1	–
1977-79	5/50	15	1.5	2.0	–
1980	5/50	7.0	0.41	2.0	–
1981-90	5/50	3.4[1]	0.41	1.0	–
1991-93	5/50	3.4	0.41	1.0	0.20
1994–98 Tier 1[2]	5/50	3.4	0.25[3]	0.4	0.08
	10/100	4.2	0.31[3]	0.6	0.10
1999-2003 NLEV[4]	5/50	3.4	0.075[5]	0.2	0.08
	10/100	4.2	0.090[5]	0.3	0.08
2004-2007 Tier 2[6] Bins (1-8)	5/50	3.4	0.75-0.100[5]	0.05-0.14	–
	10/120	0.0-4.2	0.000-0.125[5]	0.00-0.20	0.00-0.02

[1] 1981-82 model years allowed 7.0 g/mile with waiver.

[2] Standards phased in progressively between 1994 and 1997.

[3] Non-methane hydrocarbon (NMHC).

[4] Optional program.

[5] Non-methane organic gas (NMOG).

[6] Tier 2 regulation defines 8 "bins" into which vehicles can be certified to varying standards so long as the manufacturer meets an average NO_X standard of 0.07 g/mile when standards are fully implemented in 2007. Standards phased in progressively between 2004 and 2007.

California has a separate set of passenger car limits that were applied initially to 1966 model year passenger cars. Typically, California limits have preceded federal limits by a couple of years. Different federal and California limits apply for light-duty trucks, heavy-duty trucks, and buses. Chapter 5, "Gasoline Engines and Selected Systems," describes the variety of emission control devices and strategies employed to reduce emissions from gasoline-powered vehicles.

Table 2.4 shows current and future EU vehicle emissions standards. Japan's vehicle emissions standards for passenger cars and light-duty trucks are presented in Table 2.5. Straight comparisons of U.S., EU, and Japanese standards are not possible because the specified test cycles differ.

Because exhaust emissions are very dependent on how a vehicle is operated, a standard set of test conditions is needed to certify that new vehicles meet their prescribed emission

Table 2.4

European Union Emission Standards[1] Passenger Cars and Light Commercial Vehicles – Gasoline Engines

Directive	Tier	Useful Life Years/1M Miles	Effective Date for New Type Approvals	Vehicle Type[2] (Category)	Maximum Emissions, g/km (ECE 15 + EUDC / NEDC) [3,4]					
					CO	HC	NMHC[5]	HC + NO_X	NO_X	Particulates (PM_{10})[6]
91/441/EEC	Euro 1	–/80[7]	July 1992	PC (M)	2.72 (3.16)	–	–	0.97 (1.13)	–	–
93/59/EEC	(EC 93)	–/–	Oct. 1994	LCV (N Class I)	2.72 (3.16)	–	–	0.97 (1.13)	–	–
				LCV (N Class II)	5.17 (6.0)	–	–	1.40 (1.6)	–	–
				LCV (N Class III)	6.9 (8.0)	–	–	1.7 (2.0)	–	–
94/12/EC	Euro 2	–/80[7]	Jan. 1996	PC (M)	2.2	–	–	0.5	–	–
96/69/EC	(EC 96)	–/–	Jan. 1998	LCV (N Class I)	2.2	–	–	0.5	–	–
				LCV (N Class II)	4.0	–	–	0.6	–	–
				LCV (N Class III)	5.0	–	–	0.7	–	–
98/69/EC	Euro 3	5/80	Jan. 2000	PC (M)	2.3	0.20	–	–	0.15	–
2002/80/EC				LCV (N Class I)	2.3	0.20	–	–	0.15	–
			Jan. 2001	LCV (N Class II)	4.17	0.25	–	–	0.18	–
				LCV (N Class III)	5.22	0.29	–	–	0.21	–
	Euro 4	5/100	Jan. 2005	PC (M)	1.0	0.10	–	–	0.08	–
				LCV (N Class I)	1.0	0.10	–	–	0.08	–
			Jan. 2006	LCV (N Class II)	1.81	0.13	–	–	0.10	–
				LCV (N Class III)	2.27	0.16	–	–	0.11	–
Proposed	Euro 5	5/160	Sept. 2009[9]	PC (M)	1.000	0.100	0.068	–	0.060	0.0050
	Euro 6[8]		Sept. 2010	LCV (N Class I)	1.000	0.100	0.068	–	0.060	0.0050
				LCV (N Class II)	1.810	0.130	0.090	–	0.075	0.0050
				LCV (N Class III)	2.270	0.160	0.108	–	0.082	0.0050

[1] Straight comparison with the U.S. standards is impossible since the test cycles are different.
[2] PC = Passenger Car; LCV = Light Commercial Vehicle; categories and classes defined by Directives 70/156/EEC and 2001/116/EEC.
[3] New European Driving Cycle (NEDC) became effective with Euro 3.
[4] Values in parentheses are limits on conformity of production (COP).
[5] NMHC = Non-methane hydrocarbons.
[6] Applicable only to vehicles with direct-injection engine.
[7] Durability requirement for vehicles equipped with emission control devices.
[8] Basic standards for Euro 5 and 6 are the same for gasoline-powered PC and LCV; however, standards for diesel-powered vehicles differ for the two tiers.
[9] Effective date is September 2010 for PC > 2,500 kg.

Table 2.5

Japanese Vehicle Emission Specifications[1] – Gasoline Engines

Implementation Year	Vehicle Type[2]	Test Method	Units	Mean Limits[3]				
				CO	HC	NMHC[4]	NO_X	PM[5]
2000	Passenger Car	10.15 Mode	g/km	0.67	0.08	–	0.08	–
		11 Mode	g/test	19.0	2.20	–	1.40	–
	LD Truck/Bus	10.15 Mode	g/km	0.67	0.08	–	0.08	–
		11 Mode	g/test	19.0	2.20	–	1.40	–
2001	MD Truck/Bus	10.15 Mode	g/km	2.10	0.08	–	0.13	–
		11 Mode	g/test	24.0	2.20	–	1.60	–
2002	Mini Truck/Bus	10.15 Mode	g/km	3.30	0.13	–	0.13	–
		13 Mode	g/test	38.0	3.50	–	2.20	–
2005	Passsenger Car	10.15 Mode + 11 Mode	g/km	1.15	–	0.05	0.05	–
	LD Truck/Bus	10.15 Mode + 11 Mode	g/km	1.15	–	0.05	0.05	–
	MD Truck/Bus	10.15 Mode + 11 Mode	g/km	2.55	–	0.05	0.07	–
2007	Mini Truck/Bus	10.15 Mode + 11 Mode	g/km	4.02	–	0.05	0.05	–
2009	Passenger Car	10.15 Mode + JC08 Mode	g/km	0.63	–	0.24	0.05	0.005
	LD Truck/Bus	10.15 Mode + JC08 Mode	g/km	0.63	–	0.24	0.05	0.005
	MD Truck/Bus	10.15 Mode + JC08 Mode	g/km	0.63	–	0.24	0.07	0.007

[1] Straight comparison with the U.S. standards is impossible since the test cycles are different.

[2] LD = Light-Duty, GVW <1,700 kg; MD = Medium-Duty, GVW >1,700 kg and <3,500 kg.

[3] Type approval and production mean limit; for production >2,000 units per annum.

[4] NMHC = Non-methane hydrocarbon.

[5] Limits on particulate matter (PM) apply only to direct-injection, lean-burn vehicles equipped with adsorption-type NO_X reduction catalysts.

limits. The U.S. EPA requires measuring exhaust emissions while a vehicle is driven according to a specified speed-time cycle on a dynamometer. The cycle used currently is Federal Test Procedure 75 (FTP 75), which simulates a 7.5-mile urban driving route with a cold start, frequent stops, and an average speed of 19.6 mph. With the Tier 2 emission standards, the U.S. EPA phased in the SFTP (mentioned earlier). This test cycle has a higher average speed and incorporates some robust vehicle accelerations to ensure that new vehicles have acceptably low exhaust emissions under such conditions.

INSPECTION AND MAINTENANCE

In addition to establishing emission limits for new vehicles, the U.S. EPA has long recognized the importance of making sure that vehicles in use continue to function as they were designed. The emission control systems of a modern gasoline-powered vehicle are complex (see Chapter 5, "Gasoline Engines and Selected Systems"). To deliver the intended emissions performance, all of the systems must function properly. A single defect can compromise the effectiveness of several subsystems and greatly increase emissions. For example, a fault that causes an engine to operate fuel-rich will not only increase production of CO and HC in the engine but will drastically reduce the ability of the catalyst to eliminate these pollutants, thus increasing their emission by a factor of perhaps 10 or more. When this happens, one "broken" vehicle can pollute as much as 10 properly functioning vehicles can. Thus, regular inspection of an engine and its emission controls, plus prompt and effective repair of any defects, can be as important to clean air as requiring the controls initially.

In 1983, the U.S. EPA oversaw the introduction of Inspection and Maintenance (I/M) programs in a number of states with air quality problems. These mandatory programs, often referred to as *smog inspections*, require a vehicle to undergo a set of inspections to detect if its emission control systems are defective or have been tampered with. The inspections may be conducted at state-run facilities or at privately owned shops. Most involve visually checking a vehicle for obviously broken, damaged, or missing emission control components and measuring tailpipe emissions. If a vehicle fails any of the tests, its owner usually is required to have the affected items repaired, subject to certain cost limits. The 1990 Clean Air Act Amendments require a number of regions in the U.S. to implement more stringent I/M programs.[14]

Today's new vehicles have mandatory systems called *on-board diagnostics* (*OBD*) that can identify many of the problems that lead to significant increases in emissions (for example, problems with the catalytic converter or with the exhaust oxygen sensor that is part of the closed-loop A/F control system). Eventually, OBD may obviate the need for I/M programs.

VEHICLE EMISSIONS: GASOLINE EFFECTS

Changes in gasoline properties and composition can help reduce vehicle emissions. Certain gasoline modifications are very effective at enabling vehicle emission control systems to perform at their optimum levels. Other gasoline modifications are not nearly as effective at reducing emissions compared to the use of the vehicle emission control systems described in Chapter 5, "Gasoline Engines and Selected Systems." The explanations here apply chiefly to vehicles built since 1985.

Sulfur Sulfur in fuel becomes sulfur oxides in exhaust that temporarily poison the three-way catalyst. Reducing gasoline's sulfur content increases converter efficiency and decreases VOC, CO, NO_X, and toxics emissions. Sulfur also interferes with OBD catalyst monitoring sensor performance in lean-burn engines.

Although gasoline engines are not a major source of SO_2, a criteria pollutant, reducing gasoline sulfur content also reduces the direct emission of this pollutant.

Vapor Pressure Decreasing the vapor pressure of gasoline reduces evaporative VOC emissions and, to a lesser extent, can reduce exhaust VOC and CO.

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[14] Detailed information regarding I/M programs can be obtained from the U.S. EPA National Vehicle and Fuel Emission Laboratory, 2000 Traverwood Drive, Ann Arbor, Michigan 48105. Regulations regarding I/M programs can be found in the U.S. Code of Federal Regulations, Volume 40, Part 51 (40 CFR 51), Subpart S.

Oxygenates As explained earlier, CO is a result of incomplete combustion, and its formation is very dependent on A/F. In older cars, adding oxygenates to gasoline has the same effect as increasing the amount of combustion air. Oxygenated gasolines add more oxygen to a combustion chamber, make combustion more complete, and help reduce formation of carbon monoxide.

Oxygenates also tend to reduce exhaust VOC emissions somewhat, but they increase aldehyde emissions and tend to increase NO_X emissions in many vehicles. As explained previously, NO_X formation is increased by excess oxygen and higher combustion temperatures. This relationship between oxygen and increased NO_X caused California and, until recently, the U.S. EPA to limit the oxygen content of reformulated gasolines.The emissions benefit of oxygenates was greatest in pre-1990 vehicles with less effective A/F control systems than the closed-loop A/F control systems in newer vehicles. By adjusting intake A/F based on the oxygen content of exhaust, the newer systems compensate for oxygen in fuel, negating most of the emissions benefit associated with using oxygenated gasoline. The addition of adaptive learning systems has improved A/F control even more. Consequently, oxygenates seem to have little effect on exhaust emissions from newer vehicles, so long as the vehicles are operating in closed-loop mode.

Because of recent advances in automotive technology, the U.S. EPA has acknowledged that the oxygen component of RFG is not required to achieve the air quality benefits that were targeted by the Clean Air Act Amendments of 1990. With the Energy Policy Act of 2005, the U.S. Congress directed the U.S. EPA to rescind the requirement that federal RFG must contain oxygenated components. This was implemented in 2006. Although the U.S. EPA no longer requires the use of oxygenates in these gasolines, almost all gasolines used in federal RFG areas and in California are blended with ethanol and are therefore still oxygenated gasolines.

Olefins Increasing the olefin content of gasoline tends to reduce exhaust VOC emissions because olefins burn more easily and more completely than the other classes of hydrocarbons in gasoline. However, increasing olefin content also tends to increase NO_X formation. It also increases the olefin content of evaporative emissions, which is undesirable because olefins are among the most reactive hydrocarbons for ozone formation. For reformulated gasolines, the choice is to decrease olefins.

Aromatics Decreasing the total aromatics content of gasoline may reduce CO and exhaust VOC emissions, but the effects are variable and complex, probably because the aromatic compounds in gasoline are so diverse. Decreasing aromatics content reduces benzene in vehicle exhaust emissions because larger aromatic molecules are partly converted to benzene during combustion or in the catalytic converter.

Benzene Decreasing the benzene content of gasoline reduces the amount of benzene in both evaporative and exhaust VOC emissions.

Distillation Profile Temperatures Gasoline containing significant amounts of high-temperature boiling components tends to generate high VOC exhaust emissions. High-temperature boiling components are more difficult to vaporize, especially in a cold engine, making complete combustion more difficult. Thus, placing limits on the distillation profile of gasoline can help lower VOC emissions.

REFORMULATED GASOLINES

Acting on the above relationships, the U.S. EPA and CARB have established a number of regulations that control gasoline properties to reduce emissions from gasoline-fueled vehicles. The chronology is shown in Figure 2.5.

In 1992, for example, the U.S. EPA required a decrease in the maximum vapor pressure of summertime gasoline to reduce evaporative VOC emissions. It capped vapor pressure at 54 kPa (7.8 psi) in ozone nonattainment areas in the Southern and Western states, where average summer temperatures are highest, and at 62 kPa (9.0 psi) elsewhere across the nation.

That same year, California Phase 1 RFG was required throughout California. Phase 1 RFG regulations capped summertime vapor pressure at 54 kPa (7.8 psi) for the entire state, not just for ozone nonattainment areas, and forbade the use of lead-containing additives. The regulations also made the use of deposit control additives mandatory on the basis that engine intake system deposits increase emissions (see page 77). The U.S. EPA mandated that all U.S. motor gasoline contain a deposit control additive beginning in 1995.

Figure 2.5

Chronology of United States Gasoline Regulations

Federal		California
	1960	**Bromine Number** Control/reduce the formation of ozone
	1971	**Summer Vapor Pressure** Reduce evaporative hydrocarbon emissions from vehicles and fuel distribution system and reduce ozone
Unleaded Gasoline Reduce health risks from airborne lead oxides and enable use of catalytic converters on vehicles to reduce emissions	1974	
	1976 1978 1980	**Sulfur Content** Reduce sulfur oxide emissions and particulates
Summer Vapor Pressure Reduce evaporative hydrocarbon emissions from vehicles and fuel distribution system and reduce ozone	1989	
Summer Vapor Pressure Further reduce evaporative hydrocarbon emissions and ozone **Winter Oxygen** Reduce carbon monoxide emissions from vehicles in nonattainment areas	1992	**Phase 1 Reformulated (Summer Vapor Pressure)** Further reduce evaporative hydrocarbon emissions and ozone – more restrictive than federal requirements **Winter Oxygen** Reduce carbon monoxide emissions from vehicles **Leaded Fuel Banned** Help protect public health **Deposit Control Additives** Reduce carbon monoxide emissions
Phase I Reformulated Reduce ozone and toxics in nonattainment areas **Deposit Control Additives** Reduce vehicle emissions caused by fuel system deposits	1995	
Leaded Fuels Banned Help protect public health	1996	**Phase 2 Reformulated** Achieve maximum "cost-effective" reductions in vehicle emissions, including toxics
Phase II Reformulated Further reduce ozone and toxics in nonattainment areas	2000	
Tier 2 Sulfur Regulation Increases effectiveness of advanced emission control technologies	2004	**Phase 3 Reformulated** Bans MTBE and provides more refinery blending flexibility
Removal of Oxygenate Requirement for RFG No longer required to achieve benefits in newer cars **Renewable Fuels Standard** Reduce dependence on imported oil	2006	
	2010	**Phase 3 Reformulated Update** Compensate for effects of ethanol-blended gasoline on hydrocarbon and nitrogen oxide emissions
Benzene Regulation Further reduce toxics	2011	
	2012	

The year 1992 also saw implementation of the U.S. EPA's winter oxygenate program, which required the addition of oxygenates to gasoline sold in the 39 areas of the country that had not attained the NAAQS for CO. Gasoline in these areas was required to contain a minimum of 2.7 mass percent oxygen during the winter months when CO emissions tend to be highest. The four or five applicable winter months varied from area to area. Most of the original 39 areas have now attained the NAAQS for CO. However, eight areas in the Western U.S. continue to participate in the winter oxygenate program.[15]

In 1995, the U.S. EPA introduced regulations for Federal Phase I RFG to be used in the nine extreme or severe ozone nonattainment areas across the country.[16] Less severe ozone nonattainment areas were allowed to opt into the RFG program.

The U.S. EPA fixed two characteristics of Federal Phase I RFG. The average benzene content had to be less than 1 volume percent and the average year-round oxygen content had to be greater than 2.1 mass percent. Summertime vapor pressure also was limited. Otherwise, the general approach was to set vehicle emission reduction targets rather than place property or composition limits on gasoline. To make this work, the U.S. EPA provided refiners with a Simple Model, which expired in 1998, and a Complex Model, a more detailed mathematical model that relates gasoline composition to vehicle emissions. Criteria entered into the Complex Model are essentially those gasoline properties listed in the previous section. The model results are predicted levels of VOC, NO_X, and toxics emissions from a standard in-use vehicle fleet. The Complex Model helps refiners meet the prescribed vehicle emissions reductions in the most cost-effective way for each particular refinery.

In mid-1996, CARB introduced its Phase 2 RFG regulation. In its initial form, the regulation created a recipe for gasoline by specifying eight parameters of gasoline volatility and composition. It placed limits on summertime vapor pressure, benzene, total aromatics, olefins and sulfur content as well as the temperatures for the 50 percent and 90 percent evaporated points from the distillation profile. It also required a minimum oxygen content year-round.

CARB subsequently modified the Phase 2 RFG regulation, allowing refiners to certify alternative compositions through the California Predictive Model. This model is similar to the U.S. EPA's Complex Model in concept but different in some particulars. CARB's intent was to reduce the cost of producing Phase 2 RFG by allowing refiners to show that an alternative gasoline (presumably less expensive to produce) would reduce vehicle emissions at least as much as the original Phase 2 recipe. Even when the Predictive Model is used, however, the eight parameters still place limits on gasoline volatility and composition. Some of these limits are less stringent than the equivalent limits in the original recipe but are still quite restrictive.

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[15] "State Winter Oxygenated Fuel Program Requirements for Attainment or Maintenance of CO NAAQS," U.S. EPA, January 2008. Available online at *http://www.epa.gov/otaq/regs/fuels/420b08006.pdf*.

[16] The number of areas increased to 10 in 1996 with the addition of Sacramento, California, and then to 11 in 2002 with the addition of the San Joaquin Valley in California.

CARB believes that Phase 2 RFG, when first introduced, reduced vehicle VOC emissions by 17 percent, CO and NO$_X$ emissions by 11 percent, and air toxics by 44 percent, relative to California Phase 1 RFG. This was equivalent to removing approximately 3.5 million cars from California's roads.

The U.S. EPA introduced Phase II of its RFG program in 2000. The Phase II regulation continues Phase I's use of the Complex Model and retains the limits for benzene and oxygen content. However, it requires larger reductions in VOCs, toxics, and NO$_X$. (Table 2.6 summarizes the emissions reductions that must be achieved for gasolines formulated under Phase I and Phase II.) Most refiners have decreased vapor pressure, benzene content, and sulfur content as their primary strategies to meet the Phase I and Phase II emissions limits.

Table 2.6

Reductions in Vehicle Emissions for Federal Phase I and Phase II Reformulated Gasoline Programs

	Effective Date	Reduction in Emissions, % (Averaged Standard, Compared to 1990 Baseline Refinery Gasoline)		
		VOC	Toxics	NO$_X$
Phase I				
Simple Model	1995	Vapor pressure limits	≥16.5	No increase
Complex Model	1998[1]	≥17.1[2] ≥36.6[3]	≥16.5	≥1.5
Phase II				
Complex Model	2000	≥27.4[2] ≥29.0[3]	≥21.5	≥6.8

[1] Optional 1995-1997; mandatory starting in 1998.
[2] Northern states.
[3] Southern states.

California Phase 2 gasoline and Federal Phase II gasoline give roughly comparable reductions in VOCs and air toxics. With its lower sulfur content, the California fuel is believed to reduce NO$_X$ emissions by about 11 percent compared to 4 percent for the federal fuel.

California entered Phase 3 of its RFG program beginning January 1, 2004 (the regulation became effective December 31, 2003), although several refiners began producing Phase 3 RFG earlier than that. Phase 3 RFG regulations prohibit the intentional blending of methyl tertiary butyl ether (MTBE) into California gasoline. The presence of MTBE and other oxygenates has been disallowed, except for ethanol, above a *de minimis* level. California took this step because MTBE had been found in various fresh-water resources throughout the state and because it was viewed that certain amounts of MTBE could potentially affect the taste and odor of drinking water. Ethanol is now the only oxygenate that refiners can use for gasoline blending in California.

In addition to prohibiting MTBE, Phase 3 set lower limits for sulfur and benzene. Maximum average sulfur content was reduced from 30 ppm to 20 ppm, and the maximum level of benzene was reduced to 0.8 volume percent. Most other requirements for the new fuel were similar to those stipulated in Phase 2.

In 2004, the U.S. EPA began implementing Tier 2 gasoline sulfur regulations, which established new maximum standards for sulfur content in gasoline in all states except California. (California gasoline was exempted because the Phase 3 California RFG standards were already consistent with the new EPA standard.) The U.S. EPA Tier 2 gasoline sulfur regulations were phased in from 2004 to 2007. The new standard required the annual average sulfur content of gasoline produced by a refinery to be no more than 30 ppm by weight, with a cap of 80 ppm by weight on any individual batch of gasoline. By the end of 2009, gasoline nationwide must meet the 30 ppm average/80 ppm cap standards (although some small refiners are exempt until the end of 2010).

In 2007, the U.S. EPA promulgated new regulations for benzene content in gasoline as part of the Control of Hazardous Air Pollutants from Mobile Sources regulation. This regulation established an annual average maximum benzene content in gasoline of 0.62 liquid volume percent, and it becomes effective January 1, 2011. Its objective is to further reduce the toxics content of gasoline exhaust.

Also in 2007, the U.S. EPA finalized regulations for the Renewable Fuel Standard (RFS), which was authorized by the Energy Policy Act of 2005. The RFS establishes a minimum requirement for the volume of renewable fuels blended into gasoline and diesel fuel. The national minimum volume requirement started at 4.0 billion gallons per year of renewable fuel in 2006 and increases to 7.5 billion gallons per year in 2012. Each producer and importer of gasoline in the U.S. is obligated to demonstrate compliance with this requirement based on the pro rata share of gasoline it produces or imports. With the passage of the Energy Independence and Security Act of 2007, the amount of renewable fuels required was increased to 15.2 billion gallons per year in 2012 and ends with a requirement of 36.0 billion per year by 2022. The proportional requirement for cellulosic biofuel in the act begins in 2010 and scales up to 16.0 billion gallons per year by 2022.

In 2007, CARB updated its Phase 3 RFG gasoline standards to address issues related to increased hydrocarbon emissions that resulted when the state switched from MTBE-blended gasoline to ethanol-blended gasoline in 2003. The increased hydrocarbon emissions result from ethanol-enhanced permeation of seals, hoses, and gaskets in vehicle fuel systems. Based on additional vehicle testing data, the California Phase 3 RFG Predictive Model was revised to account for the increased permeation emissions, requiring refiners to reduce the volatility of their base gasoline. In addition, the maximum sulfur content standard was also reduced to further control NO_X emissions and prevent any backsliding on NO_X that might be associated with blending ethanol at higher concentrations in the future. The revised Phase 3 RFG gasoline standards will phase in beginning in 2010, with full implementation by 2012.

On January 18, 2007, the governor of California issued an executive order establishing a Low Carbon Fuels Standard (LCFS) for transportation fuels sold in California. The implementation details are under development.

European Union

In 2005, the EU initiated sulfur-content reductions in a move toward a 10 ppm maximum for all gasolines by 2009. The EU also limits aromatics to a maximum content of 35.0 volume percent. In addition to enforcing gasoline content limits, the EU helps states manage fuel availability through guidance on number and distance between refueling stations. These EU mandates are based on European Committee for Standardization specification CEN EN 228.

Japan

In 2007, Japanese Industrial Standard (JIS) K 2202 for motor gasoline limited sulfur content to 10 ppm maximum and summertime vapor pressure to 9.4 psi (65 kPa) maximum.

Abbreviations

°API	degrees API, the unit of gravity in the American Petroleum Institute system
°C	degrees Celsius, the unit of temperature in the metric (SI) system
°F	degrees Fahrenheit, the unit of temperature in the United States customary system
ABS	automatic braking system
AFNOR	L'Association Française de Normalisation
A/F	air-fuel ratio
AKI	antiknock index average of an engine fuel's research octane number (RON) and motor octane number (MON) [(RON + MON)/2, simplified to (R + M)/2]
API	American Petroleum Institute
ASTM	ASTM International (formerly American Society for Testing and Materials)
BDC	bottom dead center; the position of the piston at the bottom of its stroke
Btu	British thermal unit
C_n	carbon number, n being a variable representing the number of carbon atoms in a hydrocarbon molecule
CAI	controlled autoignition
CARB	California Air Resources Board
CARBOB	California reformulated blendstock for oxygenate blending
CCD	combustion chamber deposits
CCDF	combustion chamber deposit flaking
CCDI	combustion chamber deposit interference
CEN	Comité Européen de Normalisation (European Committee for Standardization)
CFR	Code of Federal Regulations (USA)
CGSB	Canadian General Standards Board
CO	carbon monoxide
CO_2	carbon dioxide
CPE	chlorinated polyethylene
CPFI	central port fuel injection
CRC	Coordinating Research Council (USA)
DC	deposit control
DI	driveability index
DIN	Deutsches Institut für Normung
DISI	direct injection spark ignition
DOHC	dual overhead cam
DVPE	dry vapor pressure equivalent, the value of vapor pressure obtained by a specific method
ECM	engine control module
EGR	exhaust gas recirculation
EPA	Environmental Protection Agency
Et	distillation profile volume percent evaporated at t temperature
ETBE	ethyl tertiary butyl ether
EtOH	ethanol
EU	European Union
FCC	fluid catalytic cracking
FTP 75	federal test procedure of the U.S. EPA for emissions certification of light-duty vehicles and involving a dynamometer emissions test cycle
HC	hydrocarbon

HCCI	homogeneous charge compression ignition
I/M	inspection and maintenance program, a plan for checking the condition and performance of a vehicle's emission systems
ISO	International Organization of Standardization
IVD	intake valve deposits
JIS	Japanese Industrial Standard
JSA	Japanese Standards Association
kPa	kilopascal, a unit of pressure in the metric (SI) system
LAC	lowest additive concentration (that can pass U.S. federal deposit control additive certification tests)
LCFS	Low Carbon Fuel Standard
LRP	lead replacement petrol
MIL	malfunction indicator light
mm Hg	millimeter of mercury; a unit of pressure equal to 0.001316 atmosphere
MMT	methylcyclopentadienyl manganese tricarbonyl, an antiknock compound
MON	Motor octane number
MSDS	Material Safety Data Sheet
MTBE	methyl tertiary butyl ether
NAAQS	National Ambient Air Quality Standards (USA)
NCWM	National Conference on Weights and Measures (USA)
NMHC	non-methane hydrocarbons
NMOG	non-methane organic gases
NO	nitric oxide
NO_2	nitrogen dioxide
NO_X	nitrogen oxides (or oxides of nitrogen); $NO + NO_2$
O_3	ozone
OBD	on-board diagnostics, computer-based testing system in a vehicle engine that includes an engine control module for analyzing and diagnosing emission system malfunctions
OHC	overhead cam
ONR	octane number requirement (of an engine)
ORI	octane requirement increase (of an engine)
PAH	polycyclic aromatic hydrocarbon; hydrocarbons with two or more fused aromatic rings
PCV	positive crankcase ventilation
PFI	port fuel injector
PM_{10}	particulate matter with a particle size less than 10 microns
$PM_{2.5}$	particulate matter with a particle size less than 2.5 microns
PNA	polynuclear aromatic hydrocarbon
POM	polycyclic organic matter
ppm	parts per million
psi	pounds per square inch, a unit of pressure in the U.S. customary system
RBOB	reformulated blendstock for oxygenate blending
RdON	road octane number
RD	relative density
RFG	reformulated gasoline
RFS	Renewable Fuel Standard

ROG	reactive organic gases
RON	Research octane number
rpm	revolutions per minute
RVP	Reid vapor pressure, determined only by ASTM D323
SAE	SAE International (formerly Society of Automotive Engineers)
SFTP	Supplemental Federal Test Procedure
SI	Système International d'Unités (International System of Units), metric system of measurement also, spark ignition
SIP	State Implementation Plan, a plan to improve air quality (USA)
SO_2	sulfur dioxide
SO_X	sulfur oxides; $SO + SO_2$
STC	Supplemental Type Certificate, a certificate of approval from the U.S. Federal Aviation Administration that allows modification of an aircraft from its original design; can be obtained for the use of motor gasoline in place of aviation gasoline in some older planes
TAME	tertiary amyl methyl ether
TBA	tertiary butyl alcohol
TBI	throttle body injector
TDC	top dead center; the position of the piston at the top of its stroke
TEL	tetraethyl lead, an antiknock compound
TML	tetramethyl lead, an antiknock compound
Tv	distillation profile temperature at *v* volume percent evaporated
UL	Underwriters Laboratories Inc.
U.S.	United States of America
V/L	vapor-liquid ratio
VLI	vapor lock index
VOCs	volatile organic compounds
VP	vapor pressure
WOT	wide open throttle

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