Photochemical Oxidant Air Pollution: A Historical Perspective

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Abstract

Photochemical smog first came into prominence in July 1943, in Los Angeles. In 1947, the Los Angeles County Air Pollution Control District was formed to deal with the growing smog problem, which was caused by a combination of poor atmospheric ventilation, strong solar radiation, confining topography, and generally uncontrolled pollutant emissions. In the early to mid 1950s, the basis of photochemical smog theory was set forth by Professor Arie J. Haagen-Smit of the California Institute of Technology, who concluded that ozone and other photochemical oxidants were not emitted directly, but were formed in the atmosphere when precursor emissions of oxides of nitrogen and hydrocarbons reacted with each other in the presence of sunlight. Beginning in 1959, the State of California moved to control vehicle emissions, passing a series of acts which culminated in the formation of the California Air Resources Board in 1967. On the federal level, congress passed the first Clean Air Act in 1963, with subsequent major amendments added in the 1970 Act (which also established the Environmental Protection Agency), and the 1990 Act. Although some controls had been required on motor vehicles in the 1960s, it was not until 1975 that the first catalytic converters, designed to reduce emissions of hydrocarbons and carbon monoxide appeared, with the three way catalyst (to also control oxides of nitrogen) being introduced on 1981 model vehicles. In 1976, recognizing the regional nature of photochemical smog, the four local agencies of the Greater Los Angeles region combined to form the South Coast Air Quality Management District. In the Los Angeles region, ozone concentrations showed a moderate overall decline from the late 1950s to the late 1970s, and have declined substantially from the late 1970s until the present time, even in the face of large increases in population and vehicle miles traveled. Ozone trends for the period 1986-95 are also presented for several major cities in the United States. Also discussed are current trends to incorporate market forces in the control of pollutant emissions, and the future outlook for reducing pollutant emissions still further by a combination of technological and educational means.

1. BACKGROUND: THE EARLY YEARS

1.1 Initial Awareness of Photochemical Smog

Photochemical smog first came into prominence in July 1943, in Los Angeles, California,[1] although, based on visibility statistics, it must have been present at least as early as the 1930s.[2] The area of southern California has a particularly high meteorological air pollution potential for photochemical smog and other types of air pollution, due to the high frequency of strong, low, temperature inversions, light morning wind speeds, and strong solar radiation. The high mountains fringing the area to the north and east also play a role in confining airflow so as to increase the potential for smog formation. The high air pollution potential of the area began to be realized with the sharp increase in the region's

industrial growth and resulting pollutant emissions which accompanied World War II. Postwar growth only added to the problem.

1.2 Formation of Los Angeles County Air Pollution Control District in 1947♦

In 1947, the Los Angeles County Air Pollution Control District (LAAPCD) was formed to deal with the growing smog problem,[3] replacing other agencies that had previously dealt with the problem in a less comprehensive manner. By the end of 1947, the LAAPCD had put in place the beginnings of an air pollution control program which required all major industrial sources of air pollution to obtain air pollution permits in order to continue to operate. Some of the early air pollution controls resulted in the reduction of smoke from factories and waste disposal operations, and in particular in 1958, the banning of the use of backyard incinerators. Other stationary source controls included those on gasoline composition, organic solvents, oxides of nitrogen, and sulfur compounds. [3] Ozone concentrations however continued to be high.

1.3 Development of Photochemical Smog theory by Professor Arie. J. Haagen-Smit, of the California Institute of Technology (Caltech)

In the early to mid 1950s the basis of photochemical smog theory was set forth by Professor Arie J. Haagen-Smit of the California Institute of Technology, who concluded that ozone and other photochemical oxidants were not emitted directly, but were formed in the atmosphere when precursor emissions of oxides of nitrogen and hydrocarbons reacted with each other in the presence of sunlight.[4,5] Auto exhaust, which contains both oxides of nitrogen and hydrocarbons, immediately became to be seen by many as one of the major sources of photochemical smog. Other major sources of hydrocarbons included refineries, and activities associated with the use of paints and solvents, while other major sources of oxides of nitrogen included electrical generating facilities.

2. EXPANDED EFFORTS TO ADDRESS PHOTOCHEMICAL SMOG PROBLEM

2.1 Role of Motor Vehicle in Photochemical Smog Problem: Formation of the California Air Resources Board

By the late 1950s in the Greater Los Angeles region, there had been significant reductions in emissions of oxides of nitrogen and hydrocarbons from stationary sources, but the motor vehicle still remained as a major and uncontrolled source of these precursors to ozone. Motor vehicle emissions also constituted a threat to the air quality of other regions of California, including the San Francisco Bay area, and San Diego. Beginning in 1959, the State of California moved to control vehicle emissions, passing a series of acts which

♦ Other early air pollution control districts formed in California were those in the counties of Orange (1950), Riverside (1955), and San Bernardino(1956), the San Francisco Bay Area (1956), and San Diego County (1955).

made it the first governmental entity to regulate the emissions of new automobiles, beginning with positive crankcase ventilation (PCV) controls for hydrocarbons on domestic 1963 model year automobiles. Subsequent legislation culminated in the formation of the California Air Resources Board (CARB) in 1967.[6] Among the key responsibilities of CARB were promulgating regulations for motor vehicle emissions, adopting State Ambient Air Quality Standards, and assisting and overseeing the programs of local air pollution control districts, more of which had formed by that time.[6] CARB has continued to play a major role in reducing emissions from motor vehicles by requiring industry to develop the technology to meet ever more stringent vehicle emission standards, and by funding research in a wide variety of areas dealing with mobile source emissions, and their environmental impacts.

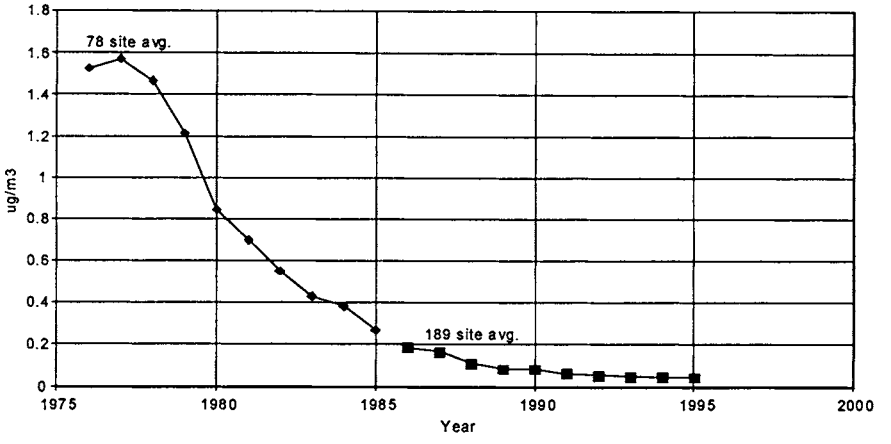
2.2 Regional Nature of Photochemical Smog

In an effort to understand more about the formation and transport of air pollution, a massive air sampling survey was carried out in the greater Los Angeles region in 1972 and 1973.[7] ♦In addition to obtaining data from a dense network of surface stations monitoring air quality and meteorological variables, fixed wing light aircraft were employed to measure the vertical and horizontal distribution of pollutant concentrations and meteorological elements over much of southern California, encompassing the four major counties of the Greater Los Angeles region. The most important conclusion of the study was that photochemical smog was a regional problem and, to be effective, air pollution control had to be carried out on a regional basis. Prior to this time, individual air pollution control agencies had tended to take a more parochial view of the problem. In 1976, recognizing the regional nature of photochemical smog, the four local air pollution control districts of the Greater Los Angeles region combined to form the South Coast Air Quality Management District (SCAQMD), and began to refer to the common airshed which they shared, as the South Coast Air Basin (SoCAB).

2.3 Development of Catalytic Converter in 1975

Perhaps no single air pollution control device has had such a favorable impact on air quality as the catalytic converter, which was first introduced on 1975 model year vehicles sold in the United States, and designed to reduce exhaust emissions of hydrocarbons and carbon monoxide. The subsequent development in 1981 model year cars of a 3-way catalytic converter, to also reduce emissions of oxides of nitrogen, benefited air quality still more. In addition to the reduction in emissions of carbon monoxide, oxides of nitrogen, and hydrocarbons, use of the catalytic converters also resulted in a dramatic improvement in lead air quality, as shown in Figure 1, since the catalytic converters required the use of unleaded gasoline. Also, the 3-way catalytic converter with its associated oxygen sensor yielded the best combination of performance , economy, and emission reductions.

♦ Other air monitoring studies carried out about the same time included the Los Angeles Reactive Pollution Project (LARPP) in 1973, and the Regional Air Pollution Study (RAPS) in St. Louis, during the period 1974-77.



Data from EPA's Nat'l Air Quality and Emissions Trend Report, 1995.

Figure 1. Lead: U.S. trends in maximum quarterly concentration, 1976-95.

2.4 Selected Federal Air Pollution Legislation

1963 Clean Air Act – Under this act, the federal government agreed to use its authority to deal with interstate air pollution problems, provide grants for program development for state and local air pollution authorities, and assume research responsibility for motor vehicle pollution.

1970 Clean Air Act Amendments – The far reaching amendments of this act, established the Environmental Protection Agency, set uniform national ambient air quality standards (NAAQS), required the submission to EPA of State Implementation Plans (SIPs) to achieve the NAAQS, and set strict emission standards for new motor vehicles.

1990 Clean Air Act Amendments – The amendments of this act were also very far reaching, including titles dealing with nonattainment, mobile sources, hazardous air pollutants, acid rain, permits, and even stratospheric ozone. With respect to ground level ozone, the act set ozone compliance deadlines ranging from November 1993 for areas in marginal attainment of the ozone standard, to November 2010 for areas with extreme ozone concentrations, the latter category applying to the Greater Los Angeles region, now referred to as the South Coast Air Basin (SoCAB). The Act also called for the use of reformulated fuels in the worst ozone areas, a reduction in gasoline volatility, and set tighter emission standards for cars and trucks.

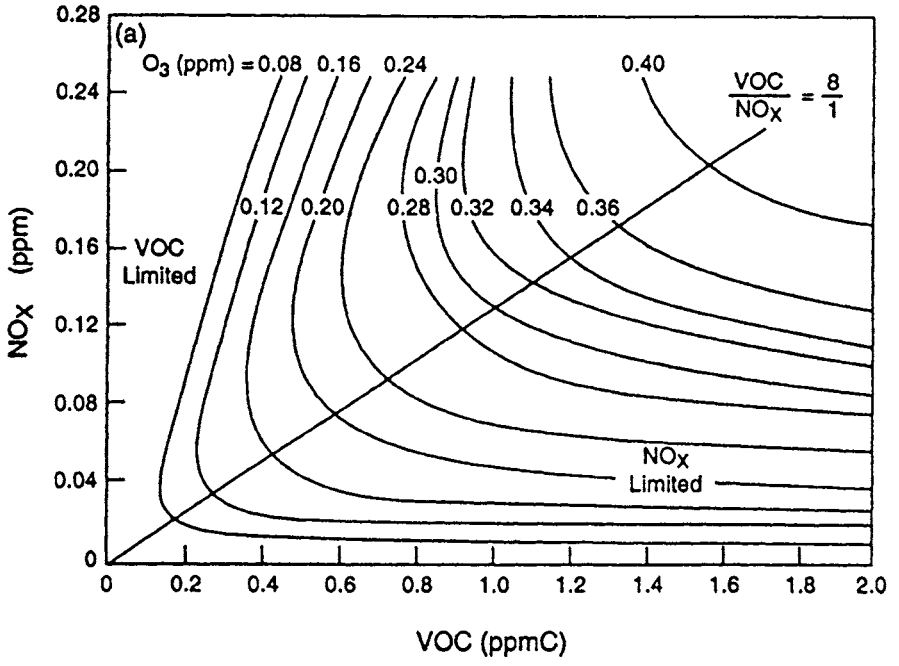


Figure 2. Empirical Kinetic Modeling Approach (EKMA) diagram and associated ozone isopleths.

3. MODELING OF PHOTOCHEMICAL SMOG

Over the years two basic approaches to modeling ozone concentrations have predominated, the empirical kinetic modeling approach (EKMA), and the grid-based photochemical model.

3.1 EKMA - The EPA first proposed the use of EKMA in the mid 1970s. It has since been updated to include more sophisticated chemistry such as the carbon bond IV mechanism, and has also been made city-specific. Figure 2 above shows a typical EKMA diagram for determining the effect of changes in emissions of volatile organic carbons (VOC)*, and oxides of nitrogen (NO_x) on ozone air quality. One's place on the chart is at the intersection of a source area's characteristic VOC/NO_x ratio during the morning hours, say 6AM to 9AM, and a characteristic maximum downwind ozone concentration later in the day. EKMA does not predict ozone maxima. Rather, the path chosen to go from the existing ozone maximum isopoleth to the desired ozone maximum isopleth determines the relative percent changes in emissions of VOCs and NO_x that are needed to accomplish the desired change in ozone concentrations. It is apparent that depending on one's position on the chart, ozone control strategies may differ considerably. For example, a position in the NO_x-limited right side of the chart, would indicate that a strategy of reducing NO_x

* Historically, in addition to being referred to as VOCs, hydrocarbon emissions which react to form ozone have also been referred to as non-methane hydrocarbons (NMHC), reactive organic gases (ROG), and non-methane organic compounds (NMOC).

emissions while leaving VOCs alone would lead to the greatest ozone improvement. The opposite situation would obtain if one's position were in the VOC limited, middle and upper portion of the left side of the chart. Indeed, in such a case, a strategy of reducing NO_x emissions alone would actually *increase* ozone concentrations. Historically, this latter situation has often been, and continues to be, a subject of controversy. Although computationally efficient, EKMA has many limitations. It is really only appropriate for regions with a well defined urban core and a relatively simple transport pathway to the location of the ozone maxima downwind.[8]

3.2 Grid-Based (Eulerian) Airshed Models

These complex models seek to represent the effect of emissions, chemistry, meteorology, and topography, on the formation and transport of ozone and its precursors, through the use of a fixed Cartesian reference system, usually consisting of cells several kilometers on a side horizontally and of varying height, depending on how many layers are being employed, and upon the mixing height of the polluted layer that is being modeled. The atmospheric dynamics are carried out within each grid cell in a repeated fashion over small increments in time, thereby simulating the formation and transport of the polluted air mass.

Grid based airshed models require detailed, accurate, spatially and temporally resolved data on emissions, meteorology, and air quality, in addition to data on topography. In recent years, the Urban Airshed Model (UAM) has been applied to a number of areas in the U.S., including Los Angeles, Sacramento, the San Joaquin Valley of California, New York, and Chicago. The Regional Oxidant Model (ROM) has been used to model ozone concentrations in the northeastern U.S., and the CIT Airshed model has been used to model photochemical smog in Mexico City.[9] One of the prime goals of each of these models is to determine the degree to which emissions of VOCs and NO_x must be reduced to achieve the desired air quality objective or standard.

Experience has shown that a more spatially and temporally detailed emission inventory, including speciated VOCs, is necessary for better model performance.[9] Also needed are better data on the meteorology, chemistry, and air quality of the polluted layers aloft, which are known to play a major role in the formation and transport of photochemical smog.[7,9] Some of the needed information is currently being pursued by a variety of special air monitoring studies.[9] In 1994, the EPA began a program to provide for enhanced monitoring of ozone and its precursors, by means of PAMS (Photochemical Assessment Monitoring Stations) for 22 ozone nonattainment areas in the U.S. rated as extreme (1 location), severe (9 locations), or serious (12 locations).[10] As of October 1996, there were 65 PAMS sites in operation, with the total expected to reach 90 sites by 1998. Some of the complexities of grid-based airshed models are shown in Figure 3.

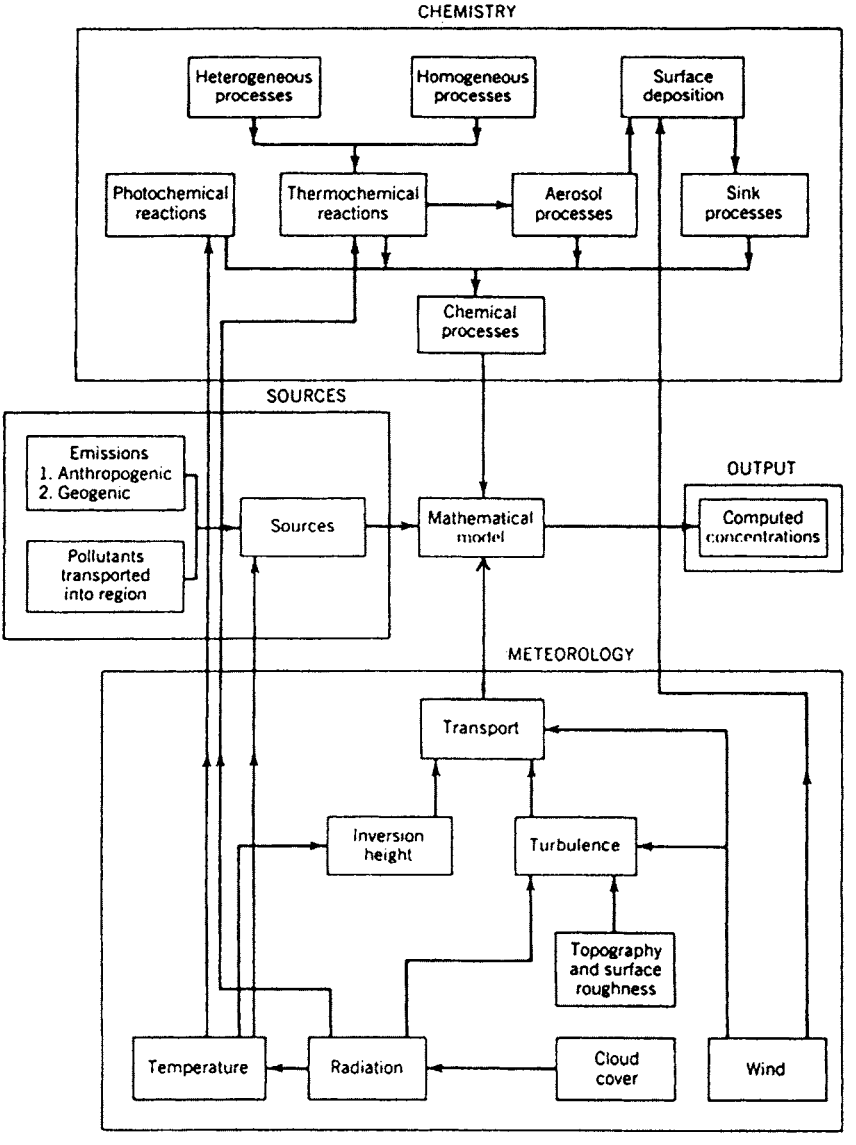


Figure 3. Elements of a typical airshed model (Source: McRae et al. [11]).

4. OZONE AIR QUALITY TRENDS

For 44 major urban areas of the United States considered as a whole, the EPA reports that there was an average decrease of about 10 percent in meteorologically adjusted concentrations over the period 1986-95.[10] This statistic refers to the 99th percentile of ozone concentrations. Figure 4 , based on EPA data,[10] shows ozone trends at four major U.S. cities during the period 1986-95. The data have been presented as three-year moving averages in order to reduce the impact of year to year differences in meteorology on the ozone trends.

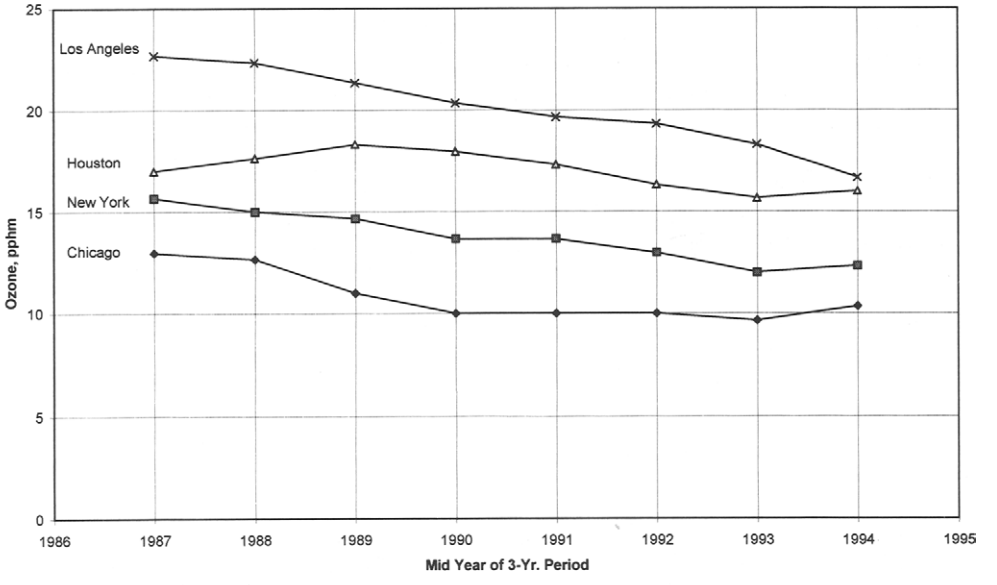


Figure 4. Ozone: 3-year moving average of 2nd highest annual 1-hr. maximum.

For the Greater Los Angeles area, based on 14 trend stations, the 3-year moving average of the 2nd highest daily 1-hour maximum ozone concentration decreased steadily over the entire period. Over the length of the period, ozone maxima decreased by 26.4 percent (from 22.7 pphm in 1986-88 to 16.7 pphm in 1993-95). In the Houston area, based on 10 trend stations, ozone maxima increased from 1986-88 to 1988-90, decreased from 1988-90 to 1992-94, and increased slightly in 1993-95. For the period as a whole ozone maxima decreased by 5.9 percent (from 17.0 pphm in 1986-88 to 16.0 pphm in 1993-95).

In the New York area, based on 4 trend stations, ozone maxima generally decreased from 1986-88 to 1992-94, before increasing slightly in 1993-95. For the period as a whole, ozone maxima decreased by 21.7 percent (from 15.7 pphm in 1986-88 to 12.3 pphm in 1993-95). At Chicago, based on 15 trend stations, ozone maxima decreased from 1986-88 to 1989-91 and showed little change thereafter. For the period as a whole, ozone maxima decreased by 20.8 percent (from 13.0 pphm in 1986-88 to 10.3 pphm in 1993-95). Of the four cities, Chicago clearly has the best ozone air quality. It is interesting to note that Los Angeles ozone maxima are now only about four percent above those of Houston, based on the latest period of 1993-95.

As would be expected, the historical data base of ozone measurements in the greater Los Angeles area is lengthy, reaching back to 1955. Although this area still exhibits the worst ozone air quality in the U.S., it is instructive to see just how much ozone concentrations have decreased since control agencies in the region geared up to respond to the problem. Figure 5 shows 3-year moving averages of the single highest 1-hour ozone concentration of the year, from 1955 through 1996. The extremely high annual ozone maxima of the early years showed little overall change from 1955-57 to 1965-67, but decreased sharply from 1965-67 to 1975-77. There was a small increase in annual ozone maxima from 1975-77 to 1978-80, but from 1978-80 until the present time there has been a long, steady decrease in ozone maxima. For the period as a whole, annual ozone maxima have decreased by 52 percent (from 56.0 pphm in 1955-57 to 26.7 pphm in 1994-96), even in the face of a doubling of population in the South Coast Air Basin.

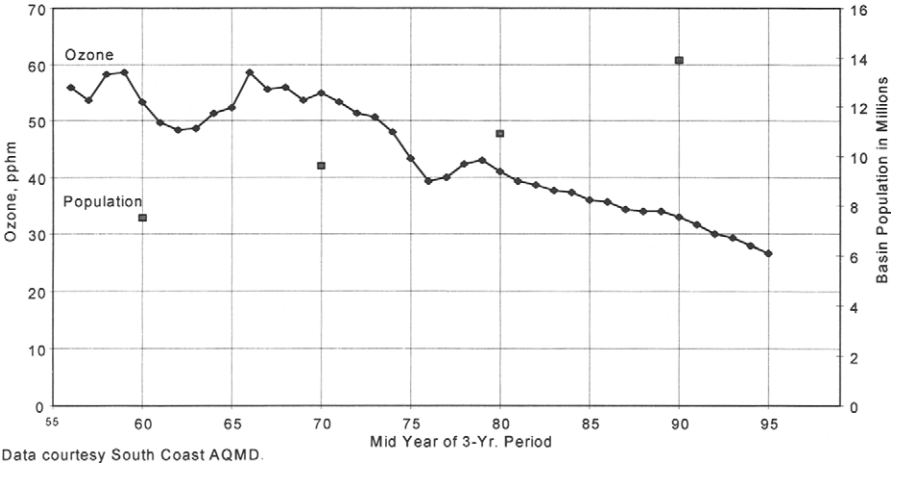


Figure 5. Ozone: 3-year moving average of annual 1-hour South Coast Air Basin maximum vs. population, 1955-96.

Further evidence of the great improvement in ozone air quality in the Los Angeles area is given in Figure 6, which shows that over the period 1976-96, based on 3-year moving averages and 17 trend stations, there has been a 100 percent reduction in the number of Basin-days♦ with ozone at or above 35 pphm, an 86 percent reduction in the number of Basin-days with ozone at or above 20 pphm, and a 48 percent decrease in the number of Basin-days exceeding the current federal standard of 12 pphm. The great improvement in ozone air quality of the South Coast Air Basin and other areas of California was brought about by increasingly strict controls on emissions of oxides of nitrogen and volatile organic carbons from both stationary and mobile sources.[12]

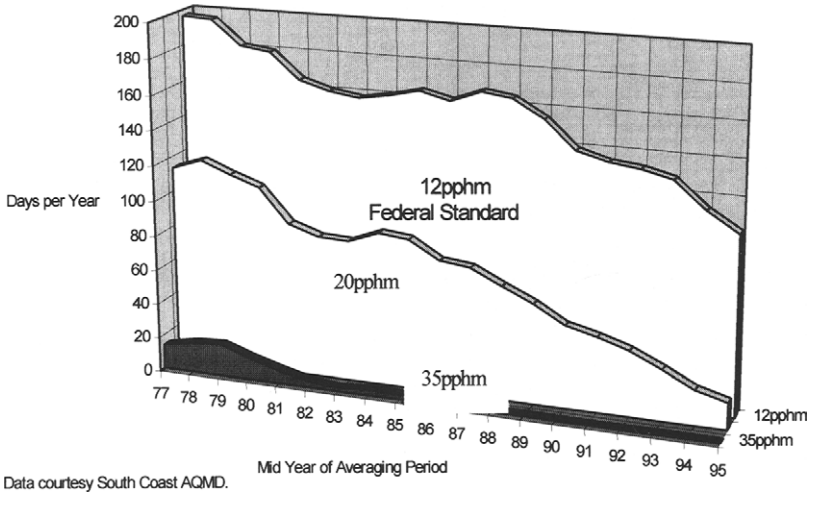


Figure 6. Ozone: 3-year moving average of Basin-days at or above indicated values.

Further improvement in U.S. ozone air quality will depend greatly on the degree to which emissions from motor vehicles can be controlled still further. One of the key areas that must be addressed is the detection and repair of vehicles which are gross emitters, that is, which emit pollutants in amounts several to many times the allowable amount for a given model year. Data from a random roadside survey of more than 11,000 vehicles in California indicate that 10 percent of the vehicles are responsible for 60 percent of fleet exhaust hydrocarbon emissions, and 10 percent of vehicles (although not exactly all the same vehicles) are responsible for 60 percent of fleet carbon monoxide emissions.[13] Another major challenge is to reduce the growth in vehicle miles traveled (VMT). In the U.S. over the period 1970 to 1995, VMT increased at a rate four times that of population (116 percent vs. 28 percent).[10]

♦ A Basin-day is defined as a day on which one or more trend stations equal or exceed a key concentration.

5. RECENT AND FUTURE DEVELOPMENTS

5.1 EPA's Proposed New Ozone Standard

On December 13, 1996, EPA announced[14] that, based on the most recent health effects research, it was proposing a change in the NAAQS for ozone from the current level of 12 pphm: 1-hour average, to 8 pphm: 8-hour average, and solicited comments on the proposal (the announcement also included a proposed change to the NAAQS for particulate matter). To insure more statistical stability in the compliance statistic, EPA also proposed that compliance be determined by taking the 3rd highest 8-hour average ozone each year, averaging the results over a 3-year period, and then comparing it to the standard. For the U.S. as a whole, the proposed standard if adopted would increase the number of ozone nonattainment counties from 106 to 336, based on statistics for the period 1993-95.[15] A final regulation is expected to be issued in July 1997, after which it will be reviewed by Congress.

5.2 Control Approaches

Throughout the history of air pollution control, one approach has dominated, that of "command and control." In this approach, regulatory agencies basically tell those in charge of emission sources the type and quantity of emissions to be reduced, and how to reduce them. This method has often proven to be successful, and for certain regions, and in many situations, may still be the preferred approach. However, when market forces can be brought to bear on the problem, air pollution controls can often be implemented at far less cost to industry, and therefore to society. For example, Title IV of the Clean Air Act Amendments of 1990, allows power plants that reduce their emissions of oxides of sulfur (SO_x) to a point below their allowable emissions, to bank the excess emission reductions, and sell them to other utilities for whom the costs of controls to meet their emission reduction targets may be very large. In this manner, the utility industry as a whole can meet its prescribed emission reduction targets, while at the time minimizing the overall costs of control.

In 1994, another market-based program, known as RECLAIM (Regional Clean Air Incentives Market) was started in the South Coast Air Basin.[16] By the early 1990s, as a result of the many rules in place for SO_x and NO_x in the SoCAB, the cost of further emission reductions had become very high, $25,000. per ton for NO_x controls at power plants, and $32,000. per ton for SO_x, for proposed catalytic crackers at refineries.[16] Clearly the time had arrived for a new approach to achieve the further emission reductions needed for these pollutants. Under RECLAIM, a facility-wide emissions limit is initially established, and then gradually reduced over a 10 year period in proportion to the emission reduction needs of the region. The operators of the facility determine how best to meet the emissions limit for the given year. Those facilities that reduce their emissions to a level below their allowable emissions, receive emission reduction credits which can then be sold on the open market. Those facilities who find it more advantageous to meet their emission limits by purchasing emission reduction credits may then do so, and thereby avoid incurring the expense and inconvenience of installing added

control equipment. RECLAIM thus allows operators of a facility to choose the path they find most advantageous, while still achieving the needed emission reductions for the region. As of early 1996 there were 353 facilities in RECLAIM[17], all emitting more than the 4 tons per year threshold needed to be included in the program. It has been estimated by the SCAQMD that controlling emissions from facilities in the RECLAIM program achieves a savings of 42 percent in average annual costs of emission reduction compared to the command and control approach.[16]

5.3 Inter-comparison of Regional Oxidant Studies

The North American Research Strategy for Tropospheric Ozone (NARSTO) has begun a project to compare methodologies, findings, and real world experiences associated with regional oxidant studies carried out in recent years.[18] This needed effort gives promise of providing valuable guidance to those charged with making key decisions on ozone air quality. The results will be presented in a paper as part of NARSTO's 1998 state-of-the science assessment.

5.4 Future Measures For Further Improving Ozone Air Quality

In order to continue to improve ozone air quality, along with other accompanying air pollution problems, it will be necessary to improve upon and go beyond what is currently being done. Possible measures, some of which are already in use in certain areas include:

- Use of lower-polluting reformulated fuels for motor vehicles.
- On-road remote sensing devices to identify gross emitting vehicles, paired with programs to require their repair.
- Breakthroughs in battery and fuel cell technology, to power electric vehicles; development of hybrid electric-gasoline powered vehicles.
- Development of paints, stains, coatings and solvents with lower or no reactive hydrocarbon emissions.
- Where appropriate, use of market forces to achieve emission reductions.
- Increased use of telecommuting and teleconferencing to reduce traffic congestion, and thereby reduce emissions.
- Employer subsidies to employees who take public transit or ride share.
- Use of public education programs to encourage a less polluting lifestyle (when millions of citizens each pollute a little less, the net emission reductions are large, and very cost-effective).

6. ACKNOWLEDGMENT

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