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Air Pollution: A Half Century of Progress

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In the 50 years since the air pollution episodes of Donora, PA and London, U.K., a great deal of progress has been made in understanding the nature and sources of air pollution and the atmospheric transport and transformation of pollutants. Also, many significant technological advances in air pollution control equipment, such as the automobile exhaust gas catalytic converter, have led to effective reduction of emissions from a variety of major pollution sources. Finally, remarkable developments in instrumentation for sampling the trace species in the atmosphere have been and continue to be made. Relatively less progress has been made in understanding the biological mechanisms by which pollutants lead to human injury and mortality. In this review the focus is on the extraordinary progress that has been made over the last half century in understanding the atmospheric nature and behavior of pollutants, both gaseous and particulate. A major breakthrough was the determination of the gas-phase chemistry of both the natural and polluted atmosphere, chemistry that leads to the formation of ozone and a vast array of oxidized molecules. The mechanisms of the oxidation of atmospheric sulfur dioxide, one of the main primary pollutants, were elucidated. Finally, the chemistry, physics, and optics of atmospheric particulate matter (aerosols) have been laid open by many stunning research achievements. Whereas 50 years ago air pollution was thought to be confined to the area around a city, it is now recognized that species emitted on one continent frequently find their way to other continents. Strategies for dealing with a truly global atmospheric backyard now represent a major challenge. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1096–1108, 2004

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Introduction

Between October 28 and 30, 1948 an atmospheric inversion, in which a warm air mass traps cold air near the surface, settled over the southwestern Pennsylvania river town of Donora. Located on the western bank of the Monogahela River, 37 miles south of Pittsburgh, Donora was home to U.S. Steel Corporation's Zinc Works and its American Steel & Wire Plant. Extraordinarily high levels of sulfur dioxide, sulfates, and fluorides built up in the air of the valley over the 3 days. By October 29, visibility had reached a point where the crowd at the high school football game could barely see the players on the field. By the time the rain cleared the air on October 30, 20 people had died and thousands of others were sickened (Snyder, 1994).

Four years later on December 5, 1952, a mixture of dense fog and sooty black coal smoke descended upon London. By December 7, visibility fell to one foot. Roads were littered with abandoned cars. When wind finally dispersed the mixture on December 9, the four-day episode had resulted in 4,000 deaths, nearly three times the normal toll during such a period. The "London Killer Fog" or "Big Smoke" as it is now known, stands as one of the deadliest environmental episodes in recorded history (Stone, 2002). (Pollution events like this gave rise to the term "smog", a combination of smoke and fog.)

At about the same time as the episodes in Donora and London, a new type of air pollution, so-called photochemical

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smog, emerged in Los Angeles. Photochemical smog is a mixture of ozone (O_3) and related compounds that are produced photochemically from directly emitted species. The process is driven by sunlight and accelerated at higher temperatures. Ozone, the principal gas-phase ingredient in photochemical smog, is not emitted from any source; it is formed entirely in the atmosphere. With its large motor vehicle population, sunny weather, and persistent temperature inversions, Los Angeles presented ideal conditions for the emergence of this new form of air pollution. Paradoxically, whereas ozone in the stratosphere protects living organisms from the harmful effects of solar ultraviolet radiation, ozone at ground level, at concentrations elevated over those of the background troposphere, can have adverse effects on plants and human health. Although data are sparse, there is evidence that regional ozone concentrations over the European continent, and perhaps the Northern Hemisphere, as a whole, may have increased by a factor of two or more this century (Volz and Kley, 1988).

The study of atmospheric chemistry as a scientific discipline can be traced to the 18th Century when world-renowned chemists such as Joseph Priestley, Antoine-Laurent Lavoisier, and Henry Cavendish investigated the chemical composition of the atmosphere. Through their efforts, and those of other prominent scientists in the 19th Century, the identity and concentration of the major components of the atmosphere (nitrogen, oxygen, water, carbon dioxide, and the rare gases) were established. In the late 19th and early 20th Centuries, the focus shifted from identifying the major atmospheric constituents to the trace species, those constituents having mole fractions less than a few parts per million parts air. As modern chemical analytical techniques emerged, the atmosphere was revealed to contain a myriad of trace species, the presence of which can be attributed to a complex array of geological, biological, chemical, and, in many cases, anthropogenic processes. With their identification, these trace species were discovered to have a disproportionately large impact on the atmosphere and the environment in general. Observations have now demonstrated irrefutably that the chemistry of the atmosphere is changing on local, regional, and global scales.

Anthropogenic emissions are minute compared to the mass of the atmosphere itself. How, one might ask, can such small relative emissions exert such noticeable effects on the atmosphere? First, certain trace species act as catalysts for chemical changes; small amounts can lead to large effects. Second, if a species is not removed efficiently from the atmosphere, then its emissions, even if small, over a long period of time can add up to a substantial amount. Third, certain molecules absorb radiation in so-called window regions of the solar and infrared spectra, where even small amounts can lead to significant radiative impacts.

In the 50 years since Donora and London, enormous progress has been made in understanding and controlling air pollution. As a discipline, chemical engineering has played an instrumental role in this progress. The predominance of air pollution emissions result from combustion processes. The detailed chemistry and physics of combustion and how the combustion system itself influences fuel burning must be understood to minimize emissions. Conception and design of methods for the removal of unwanted substances from emission gas streams before their release to the atmosphere are core problems in traditional chemical engineering. Once compounds are released, the atmosphere becomes a giant chemical reactor. Predicting atmospheric concentration levels requires understanding of how species are transported and transformed in the atmosphere, and how they are ultimately removed from it.

Table 1. Some Milestones in Air Pollution History

1948	Air pollution episode in Donora, Pennsylvania kills 20 people and makes 40 percent of the town's 14,000 inhabitants ill.
1952	Sulfur and soot-laden smog covers London and is responsible for 4,000 deaths over a two-week period.
1955	Congress passes Air Pollution Control Act which identified air pollution as a national problem.
1963	Congress passes Clean Air Act of 1963 which set emissions standards for stationary sources such as power plants and steel mills. Amendments were passed in 1965, 1966, 1967, and 1969, authorizing the Secretary of Health, Education, and Welfare to set standards for motor vehicle emissions.
1970	Congress passes Clean Air Act of 1970, the first substantive environmental statute enacted by Congress. The law established National Ambient Air Quality Standards (NAAQS) and set new limits on emissions from stationary and mobile sources. Also allowed states to establish their own stricter standards, which California did.
1975	Catalytic converter introduced into vehicle fleet. Cuts hydrocarbon and carbon monoxide emissions by 96 percent and nitrogen oxides by 75 percent.
1977	Revised Clean Air Act Amendments passed by Congress, providing more time for areas with more serious air quality problems to comply with standards.
1988	EPA establishes Indoor Air Division of the Office of Air and Radiation to address indoor air quality issues.
1990	Congress passes Clean Air Act of 1990, tightening automobile emissions standards, encouraging the use of low-sulfur fuels, and mandating installment of Best Available Control Technology.
1997	EPA strengthens the standard for airborne particulate matter.
2000	Tier 2 program, will be phased in starting in 2004, when refiners must produce low-sulfur fuel for passenger vehicles. Tier 2 also sets tailpipe emission standards for all classes of passenger vehicles, including sport utility vehicles and light-duty trucks.
2001	Supreme Court supports health-based air pollution standards when it rejects challenges to the new standard for particulate matter.
2001	The Heavy Duty Diesel Rule will require significant future reductions in highway diesel engine particulate matter emissions. It will also require diesel oil refiners to reduce most sulfur from diesel fuel by 2006 in preparation for new engines in 2007.
2002	Legislation (AB 1493) passed in California that requires automakers to reduce greenhouse gases from motor vehicles.
2002	California adopts more stringent particulate matter standards for PM_{10} and $PM_{2.5}$.

The legislative history of air pollution regulation at the state and federal levels in the United States, which began shortly after the Donora tragedy and the identification of the Los Angeles smog, comprises a complex labyrinth of laws and judicial decisions. Table 1 summarizes some of the milestones in air pollution legislation in the United States over the last 50 years. Space does not permit us to document changes in air quality and visibility in the U.S. over the past decades; these data are available on the website of the U.S.E.P.A. (www.epa.gov), as well as those of state air pollution control agencies.

A review of progress in understanding of air pollution could address a number of fronts: improvements in combustion systems, new advances in emission controls (both stationary and mobile source), increased knowledge of health effects of pollutants, developments in instrumentation and sampling technologies, and understanding of the atmospheric transport and transformation of emitted species. It is this last issue on which we will focus here. Underlying the attempt to control air pollution is the fundamental question – How are atmospheric concentration levels related to source emissions? We will provide a historical survey of advances toward answering this question over the last 50 years.

Ozone and Radical Chemistry

In the troposphere, for every 100,000,000 molecules, about 3.5 of them are, on average, O_3. Ground-level O_3 mole fractions, or so-called mixing ratios, in the U.S. range from 20 to 60 parts-per-billion by volume (ppbv). Values exceed 100 ppbv in urban areas and regions downwind of urban complexes. Ozone concentrations in urban plumes tend to reach a maximum 50 to 100 km downwind of the city center. However, because ozone has a lifetime of several days, elevated levels can persist much farther downwind. In addition to urban plumes, elevated ozone levels can extend over broad regions. Region-wide events, in which a stagnant high-pressure system produces several days of high temperatures and stagnant conditions, occur relatively frequently over the entire eastern U.S. One of the most notable was an event that occurred during the second week of June, 1988; ozone mixing ratios exceeding 90 ppbv were observed at every surface monitoring site in an area extending from Maine to Virginia to Ohio. Even higher values were found in the cities of the northeast corridor. Ozone levels exceeding 200 ppbv are, these days, relatively rare and constitute a severe air pollution episode. The highest recorded hourly-average O_3 mixing ratio in North America was apparently 680 ppbv, in downtown Los Angeles in 1955 (NARSTO, 2000). The current U.S. National Ambient Air Quality Standard for O_3 is an 8-h average of 80 ppb (The actual air quality standard for O_3 is somewhat more complicated. One must take the fourth-highest 8-h concentration for each of the three consecutive years at each monitoring location, take the average and compare it to 80 ppbv.)

With the emergence of Los Angeles photochemical smog in the late 1940's and early 1950's and the identification of O_3 as its principal ingredient, the effort began to understand the nature of this new form of air pollution. Dr. Arie J. Haagen-Smit, a professor of biology at the California Institute of Technology, found that his plants were being harmed by the Los Angeles air and set out to understand why. In two pioneering articles published in *Industrial and Engineering Chemistry*, he identified ozone as the principal component of photochemical smog and postulated that a free-radical chain reaction mechanism involving organics and oxides of nitrogen was responsible for hydrocarbon and oxidation, and O_3 buildup (Haagen-Smit, 1952; Haagen-Smit et al., 1953). Although the species oxidizing the hydrocarbons and other organic compounds was unknown, Haagen-Smit did deduce the critical fact that nitrogen oxides play the role of a catalyst in ozone formation. In 1961, the renowned photochemist, Philip A. Leighton of Stanford University, published a comprehensive monograph, *Photochemistry of Air Pollution* (Leighton, 1961). He exhaustively surveyed known reactions of oxygen atoms, ozone, nitrogen oxides, and organic free radicals, but the dominant mechanism of atmospheric hydrocarbon oxidation still remained elusive. Although it was long known that hydroxyl (OH) radicals react rapidly with hydrocarbons, whether OH radicals played any significant role in the chemistry of the atmosphere was unknown. On page 226 of his monograph, Leighton stated, "Unfortunately, little may be said as to the rate at which hydroxyl radicals are produced in polluted air."

The hint came in 1969, and then the breakthrough came in 1971. With information on the ^{14}C content of atmospheric CO, Bernard Weinstock of Ford Motor Company deduced that the atmospheric lifetime of CO was 0.1 year, a value far smaller than what had been thought up to that time (Weinstock, 1969). The short residence time implied that CO is being removed from the atmosphere far faster than any known mechanism could explain. Noting that a likely process for conversion of CO to CO_2 in the stratosphere is

$$CO + OH \rightarrow CO_2 + H$$

Weinstock suggested that the same reaction could be an effective removal mechanism for tropospheric CO and noted that to maintain the needed OH levels would require some kind of regenerative chain mechanism for tropospheric OH, although he did not know what that mechanism was. It was known that photodissociation of O_3 in the wavelength range of 290 to 340 nm produces excited atomic oxygen $O(^1D)$, a small fraction of which reacts with atmospheric water vapor to produce OH radicals. Hiram ("Chip") Levy, then at the Smithsonian Astrophysical Observatory in Cambridge, Massachusetts, showed that even that small fraction is sufficient to produce OH radicals in the atmosphere at a rate exceeding 10^5 molecules cm^{-3} s^{-1}, making OH the dominant oxidizing free-radical in the troposphere (Levy, 1971).

The atmosphere's source of energy for driving chemical reactions is the sun, and all of atmospheric chemistry begins with photolytic processes. The vast majority of atmospheric chemistry involves free-radical reactions, and free-radical kinetics is the key to understanding atmospheric chemistry. With the recognition of the central role of the OH radical in tropospheric chemistry, atmospheric chemical reaction mechanisms for hydrocarbon oxidation and ozone formation began to be developed. Levy, in his 1971 article, suggested a mechanism for atmospheric methane chemistry, which governs that of the background troposphere. The first general mechanism for the chemistry of an atmosphere containing mixtures of organic species, such as in urban air, was formulated by Hecht and Seinfeld (1972). Since that early work, our understanding of the chemistry of the troposphere has expanded and deepened enormously (Atkinson et al., 1997). Highly detailed atmospheric chemical mechanisms now exist, the most comprehensive being the master chemical mechanism (MCM) developed in the U.K. by Jenkin et al. (1997) and Derwent et al. (1998). The MCM includes more than 2,400 chemical species, and over 7,100 chemical reactions for 120 of the most important volatile organic compounds. A mechanism of such large size is not practical for use in a three-dimensional (3-D) atmospheric model; therefore, aggregated mechanisms have been developed. Following from the original Hecht-Seinfeld mechanism, some milestones in atmospheric gas-phase mechanisms include the Carbon Bond Mechanism IV (Gery et al., 1989), the Regional Acid Deposition Model Mechanism (Stockwell et al., 1990), the Regional Atmospheric Chemistry Mechanism (Stockwell et al., 1997), and the series of mechanisms developed at the Statewide Air Pollution Research Center at the University of California, Riverside (Carter, 1990, 1999).

Predicting how atmospheric levels of pollutants will respond to a change in source emissions requires a 3-D atmospheric chemical transport model (CTM). Now, such models are used routinely to simulate regions ranging from the urban airshed to the global troposphere (Seinfeld and Pandis, 1998; Jacobson, 1999). The first 3-D CTM was developed in 1973 to simulate photochemical smog formation in the Los Angeles air basin (Reynolds et al., 1973, 1974; Roth et al., 1974). This initial work led to several generations of models for urban and regional air quality (Seinfeld, 1988). A major figure in the development and application of regional-scale CTMs is Gregory Carmichael of the University of Iowa. 3-D models of global tropospheric chemistry appeared in the early 1990s.

Tropospheric Ozone. Ozone in the troposphere is generated from two major classes of precursors: volatile organic compounds (VOCs) and oxides of nitrogen (NO_x, which denotes the sum of NO and NO_2). As noted earlier, the process of ozone formation is initiated by the reaction of the OH radical with organic molecules. The subsequent reaction sequence is catalyzed by NO_x, in an interwoven network of free-radical reactions. Most of the direct emission of NO_x to the atmosphere is in the form of NO. NO_2 is formed in the atmosphere by conversion of NO. The two oxides of nitrogen are generally grouped together as NO_x because interconversion between NO and NO_2 is rapid (with a timescale of about 5 min) compared to the timescale for organic oxidation (one or several hours). NO_x mixing ratios range from 5 to 20 ppbv in urban areas, about 1 ppbv in rural areas during region-wide episodes, and from 10 to 100 parts per trillion by volume (pptv) in the remote troposphere.

In the remote troposphere ozone formation is sustained by the oxidation of carbon monoxide (CO) and methane (CH_4), each through reactions with OH. Both CO and CH_4 are long-lived species, with atmospheric lifetimes against OH reaction of about 2 months and 9 years, respectively. Ozone formation in the urban and regional atmosphere is driven by volatile organic compounds emitted from anthropogenic and biogenic sources. These include alkenes, aromatics, and oxygenated organic species.

Because there are two classes of precursor compounds involved in tropospheric ozone formation, volatile organic compounds (VOCs) and oxides of nitrogen (NO_x), the key question relating to ozone reduction is how reductions in VOC and NO_x affect ozone levels. At first glance, one might think that the reduction of both precursors would lead to ozone decrease. The chemistry of ozone formation is, however, exquisitely nonlinear, and early laboratory chamber experiments showed that, for certain ranges of concentrations, ozone actually increases as NO_x is reduced. This nonlinear behavior means that designing ozone reduction strategies is not straightforward. The earliest ozone control strategies adopted in the U.S. were based on VOC-only control, because it was known that when NO_x levels are relatively high, VOC control leads to ozone reduction. Also, VOC reductions tend to be less costly than NO_x reductions, so picking the "low hanging fruit" was an effective early strategy.

A point was reached in the late 1980s when regional ozone episodes, such as that described earlier in the northeast U.S., were unaffected by continued VOC control. In 1989 the National Research Council (NRC) convened a panel of scientists to reassess the nation's strategy for ozone control. The report the panel issued, *Rethinking the Ozone Problem in Urban and Regional Air Pollution* (Seinfeld et al., 1991), showed that NO_x control was critically needed in many areas of the country. This study led to a re-evaluation of ozone control in the U.S. by the Environmental Protection Agency and to the eventual formation of the North American Research Strategy for Tropospheric Ozone (NARSTO, 2000).

A realization also emerged in the late 1980s concerning the sources of atmospheric VOCs: there are significant emissions of VOCs from vegetation. This realization played an important role in the NRC study. The biogenic hydrocarbon emitted in the largest quantity is isoprene (C_5H_8); moreover, from the viewpoint of ozone formation, isoprene is one of the most reactive VOCs in the atmosphere. Biogenic VOC emissions often equal or exceed anthropogenic VOC emissions on the regional scale. The significance of biogenic VOCs with respect to ozone formation lies in their impact on ozone reduction strategies. In regions with significant VOC emissions, the atmospheric organic loading is larger than that based on anthropogenic VOCs alone. As we will see, such regions are less sensitive to VOC control and more sensitive to NO_x control. A pioneering article by Chameides et al. (1988) showed how isoprene levels would affect attempts to control ozone in Atlanta.

Ozone Chemistry. What is the source of the nonlinearity in the VOC-NO_x-O_3 system? How can understanding of the system lead to effective control strategies? The ozone formation process begins with the reaction of a volatile organic compound or CO with the OH radical. For a saturated hydrocarbon, OH abstracts a hydrogen atom from the molecule, which then acquires O_2 to form a radical of the form RO_2

$$RH + OH \xrightarrow{O_2} RO_2 + H_2O \tag{1}$$

For CO, the analogous reaction is

$$CO + OH \xrightarrow{O_2} HO_2 + CO_2 \tag{2}$$

This is followed by reactions of HO_2 and RO_2 with NO

$$RO_2 + NO \xrightarrow{O_2} R'CHO + HO_2 + NO_2 \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

where R$^{'}$CHO denotes an oxygenated organic species, typically an aldehyde or ketone. Reactions 3 and 4 convert NO to NO_2. The NO_2 readily photolyzes

$$NO_2 + h\nu \rightarrow NO + O \qquad (5)$$

and the oxygen atom immediately combines with O_2 to form O_3; this is, in fact, the only reaction producing O_3 in the atmosphere. As long as the mixing ratio of NO_x exceeds about 0.5 ppbv (typical of urban and polluted rural sites in the eastern U.S. and Europe), Reactions 3 and 4 are the dominant reaction paths for the peroxy radicals HO_2 and RO_2.

The odd hydrogen radicals, $HO_x = OH + HO_2 + RO_2$, are eventually removed by reactions that produce peroxides and nitric acid

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (6)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (7)$$

$$OH + NO_2 \rightarrow HNO_3 \qquad (8)$$

When ambient NO_x mixing ratios are large, Reaction 8 is the predominant loss mechanism for both HO_x and NO_x. This situation is referred to as NO_x-saturated conditions. Under low NO_x conditions, the main HO_x removal occurs by peroxy-peroxy Reactions 6 and 7. This regime is called NO_x-sensitive conditions.

Whether the atmosphere is in an NO_x-saturated or NO_x-sensitive state is critical in determining how O_3 formation responds if NO_x levels change. At high VOC/NO_x ratios, at a given value of VOC, the rate of O_3 production increases with increasing NO_x. Eventually, as NO_x increases, the O_3 production rate reaches a maximum and then decreases as NO_x concentrations are increased further. The point of maximum O_3 production defines the boundary between NO_x-sensitive and NO_x-saturated regimes. In an NO_x-sensitive regime O_3 can be reduced only by reducing NO_x. Ozone in an NO_x-saturated region can be reduced by reducing VOC. Ozone reduction from an NO_x-saturated regime can also be achieved by reducing NO_x, but only by reducing it to extremely low levels (crossing the maximum and bringing the atmosphere into an NO_x-sensitive state).

The split of O_3 formation into NO_x-saturated and NO_x-sensitive regimes can be understood from the cycle of odd hydrogen radicals. When Reaction 8 is the dominant sink of HO_x, the ambient level of OH decreases as NO_x increases and is largely unaffected by increasing VOCs. When the dominant sink for HO_x is Reactions 6 and 7, the sum $HO_2 + RO_2$ is relatively insensitive to changes in VOCs or NO_x. The rate of O_3 formation, which is approximately equal to the sum of Reactions 3 and 4, increases with increasing NO_x and is largely independent of VOC. This is the NO_x-sensitive region. The concept of NO_x-saturated and NO_x-sensitive regimes plays a key role in designing ozone control strategies.

Ozone Production Efficiency. The concept of ozone production efficiency, introduced by Liu et al. (1987), Lin et al. (1988), and Trainer et al. (1993), has proven very useful in evaluating the state of the atmosphere with respect to its ability to produce ozone. The ozone production efficiency (OPE) is defined as the number of molecules of O_3 produced per molecule of NO_x. Recalling that NO_x is the catalyst for O_3 formation, and that NO_x is removed by nitric acid formation, Reaction 8, the OPE represents the number of O_3 molecules produced before a molecule of NO_x is lost to nitric acid. In theory, the OPE is the ratio of the rates of Reactions 1 + 2 to that of Reaction 8. (Actually, NO_x is also removed by other nitrate-forming reactions so its rate of removal is generally somewhat larger than that from Reaction 8 alone.) Under rural conditions, at NO_x about 1 ppbv, OPE values can be close to 10. Under more heavily polluted conditions, say 10 ppbv NO_x, OPEs tend to lie in the range of 3 to 5. Atmospheric measurements that lead to an estimate of a region's OPE can aid in determining how effective a precursor reduction strategy will be.

We now essentially understand the relationship between urban and regional ozone levels and its precursors. The challenges lie in developing cost-effective control measures that will continue to reduce ozone levels.

Case Study: Houston. Houston, a city of about 4 million people, has, in the last decade, experienced among the highest O_3 concentrations recorded in the U.S. During August - September 2000, the 2000 Texas Air Quality Study (www.utexas.edu/research/ceer/texaqs/) was carried out to diagnose the chemical nature of the Houston atmosphere. The study, co-directed by David Allen at the University of Texas, included extensive air sampling from ground- and aircraft-based platforms. Plumes from a variety of anthropogenic sources were tracked, including power plants, traffic, and the Houston petrochemical complex, one of the largest in the world. One surprising finding was unexpectedly large amounts of reactive alkenes, chiefly ethene and propene, being emitted from the petrochemical source complex. Ethene and propene are potent ozone-forming molecules, and ozone was observed to form rapidly and in high yield downwind of this complex; ozone production efficiencies between 10 and 18 molecules of ozone per molecule of NO_x removed were measured (Daum et al., 2003). The high alkene emission rates had not been reflected in the existing Houston VOC emissions inventories. The 2000 Texas Air Quality Study stands as a watershed application of combined field measurements and atmospheric modeling in diagnosing a major urban air pollution problem.

Atmospheric Sulfur

One of the earliest identified gas-phase pollutants was sulfur dioxide (SO_2), formed in the burning of sulfur-containing fuels. Gaseous SO_2 is an air pollutant in its own right, but SO_2 is effectively oxidized in the atmosphere, as evidenced by the widespread presence of sulfate particles. The quantity of particulate sulfate in the atmosphere cannot be explained by direct emission of sulfate itself, and must result from oxidation of SO_2.

Oxidation of Sulfur Dioxide. As with virtually every other molecule in the troposphere, sulfur dioxide reacts with the OH radical; this route leads to sulfuric acid, the formation of which is followed by rapid transfer of H_2SO_4 to the aerosol phase as a result of its very low vapor pressure. The rate constant for the SO_2 - OH reaction at 298 K is 1.5×10^{-12} cm^3 molecule^{-1}s^{-1}, which, at a typical atmospheric concentration of OH of 10^6

molecules cm^{-3}, leads to a mean lifetime of a vapor molecule of SO_2 against OH reaction of about 10 days. On the basis of observed amounts of particulate sulfate, this rate of reaction is simply too slow to account for all the particulate sulfate; other mechanisms must be at work.

Traditionally, clouds were not envisioned as a medium for chemical reactions. In the search for the "missing" conversion path from sulfur dioxide to sulfate, however, it was recognized that cloud droplets are microscopic beakers in which aqueous-phase chemistry can occur. It is now known that of all heterogenous processes in the troposphere, the most important involve clouds. Clouds contain the overwhelming amount of atmospheric liquid water (and ice), and present a large surface and volume ratio for mass transfer from the gas phase. The ratio of the amount of liquid water associated with clouds to that associated with aerosol particles per unit volume of atmosphere (when clouds are present) is $\sim 10^4$. The sequence of steps involved in the ultimate oxidation of a dissolved gas in cloud droplets is familiar to any chemical engineer: diffusion from the bulk gas phase to the droplet surface, uptake of the gas molecule into the droplet, simultaneous diffusion and chemical reaction of the dissolved molecule within the drop, followed by the reverse processes if the products of reaction are volatile species (the application of these principles to liquid-phase atmospheric reactions was made in an important article by Schwartz and Freiberg, 1981).

Gas-liquid equilibrium for a species A in an aqueous medium is described by its Henry's Law constant, H_A (M atm^{-1}). For example, the value of H_{SO_2} at 298 K is 0.034 M atm^{-1}. When SO_2 dissolves in water, it forms first the solvated form, $SO_2 \cdot H_2O$, which then ionizes to H^+ and, HSO_3^-, followed by further dissociation of the bisulfite ion: $HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$. The total amount of dissolved SO_2 in any of the three forms, as well as the relative quantities of $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-}, depends strongly on the pH of the solution. As pH increases, the total amount of dissolved sulfur increases dramatically (Seinfeld and Pandis, 1998).

Dissolution of SO_2 in cloud droplets produces *sulfite* (sulfur in the +4 oxidation state, S(IV)); however, atmospheric measurements indicate that particulate sulfur occurs in the form of *sulfate* (sulfur in the +6 oxidation state, S(VI)). If a path of conversion to sulfate in cloud droplets occurs, sulfite has to be oxidized to sulfate. When considering atmospheric gas-phase species capable of oxidizing aqueous-phase sulfite and having a sufficiently large Henry's Law constant, hydrogen peroxide (H_2O_2) emerges (Martin and Damschen, 1981; McArdle and Hoffmann, 1983; Munger et al., 1983). With an H_A value of 7.1×10^4 M atm^{-1} at 298 K, H_2O_2 is among the most soluble gases in the atmosphere, and, for pH values less than about 5, the reaction of dissolved H_2O_2 with dissolved S(IV) is very effective. Whereas the characteristic time for gas-phase oxidation of SO_2 by OH is of the order of 10 days, that for aqueous-phase oxidation of dissolved S(IV) by H_2O_2 can be the order of minutes. Droplets themselves do not always leave the atmosphere as precipitation. In fact, on average, 9 out of 10 clouds evaporate before precipitating, leaving the dissolved solutes in cloud drops as residual atmospheric particles. With this, the puzzle of SO_2 oxidation to aerosol sulfate was solved.

Most atmospheric species are soluble to some extent, and the liquid-phase reactions that are possible lead to a diverse spectrum of products. Sulfur dioxide is not particularly soluble in pure water, but the presence of other dissolved species such as H_2O_2 or O_3 that convert sulfite to sulfate displaces the dissolution equilibrium for SO_2, effectively enhancing the solubility of SO_2. Chemical reaction mechanisms in cloud water involving both inorganic and organic constituents have now grown to hundreds of reactions, including oxidation of SO_2 by dissolved ozone, but the H_2O_2 oxidation of dissolved sulfur remains the most important aqueous-phase route for conversion of SO_2 to sulfate. Globally, it is estimated that 15% of SO_2 oxidation occurs by gas-phase OH reaction and 85% by all aqueous-phase processes combined. Of the aqueous-phase processes, about 76% occurs by H_2O_2 oxidation and about 24% by ozone oxidation (Liao et al., 2003). An implication of the dominant role played by H_2O_2 in atmospheric sulfate formation is that the formation of sulfate may be limited by the supply of H_2O_2 rather than the amount of SO_2. The atmospheric chemistry of H_2O_2 is closely linked to that of O_3 through Reaction 6.

In summary, droplets can both alter the course of gas-phase chemistry through the uptake of vapor species and act as a medium for the production of species that otherwise would not be produced in the gas phase, or would be produced by different paths at a lower rate in the gas phase.

Acid Rain. Deposition to the earth's surface is the way in which the atmosphere cleans itself. There are two types of deposition mechanisms: dry deposition, that is, uptake of gases or particles at the Earth's surface (soil, water, or vegetation), and wet deposition, consisting of two components: rainout, in which aerosol particles act as cloud condensation nuclei (CCN), form cloud droplets, and are removed when cloud droplets coalesce into rain drops and fall to the ground; and washout, in which rain drops remove aerosol particles by impaction as they fall through the air. Wet deposition can be measured conveniently by sampling precipitation; dry deposition is a slower process that cannot be easily measured. It is possible, however, to measure the downward flux of airborne materials by micrometeorological methods that do not interfere with the natural characteristics of the surface.

The term "acid rain" is used loosely to describe the precipitation of acidic substances from the atmosphere. Acid deposition, however, refers to the transfer of acidic compounds to the Earth's surface by both wet and dry processes. Rain is naturally acidic; dissolved CO_2 alone produces a pH of 5.6. Because of other naturally occurring acids, clean rain throughout the world is generally considered to have a pH of about 5.0. "Acid rain" has a pH of about 4.0 or a bit higher. Rainwater acidity beyond that naturally occurring is caused mainly by dissolved sulfur and nitrogen compounds. The British chemist, Angus Smith, discovered acid rain in 1852. He published a book, *Air and Rain*, in 1872, but it drew little notice. Although acidification of fresh waters was noticed in southern Norway in the 1920s, it was not until the 1950s that acid precipitation emerged as an environmental issue. Acidification of surface waters and its effect on fisheries has been widely reported in Europe since the 1970s. In the 1980s a major national effort was mounted, the U.S. National Acid Precipitation Assessment Program (NAPAP) (1991), which included the development of detailed atmospheric models for acid precipitation, and an analysis of sources. Efforts to control acid precipitation in the U.S. focused primarily on SO_2 from power plants, which account for about 70% of SO_2 emissions. Legislation passed in

1990 created a two-phase program designed to reduce SO_2 emissions from power plants 50% from the 1980 level by 2010.

Particulate Matter

Particles in the atmosphere arise from natural sources, such as wind-borne dust, sea spray, and volcanoes, and from anthropogenic activities, such as combustion of fuels. Although an aerosol is technically defined as a suspension of fine solid or liquid particles in a gas, common usage refers to the aerosol as the particulate component only. Emitted directly as particles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosol), atmospheric aerosols are generally considered to be the particles that range in size from a few nanometers to tens of micrometers in diameter. Once airborne, particles can change their size and composition by condensation of vapor species or by evaporation, by coagulating with other particles, by chemical reaction, or by activation in the presence of water supersaturation to become fog and cloud droplets. Particles smaller than 1 μm dia. generally have atmospheric concentrations in the range from around 10 to 1,000's per cm^3; those exceeding 1 μm diameter are usually found at concentrations less than 1 cm^{-3}. Particles with diameters larger than 2.5 μm are operationally identified as coarse particles, whereas those with diameters less than 2.5 μm, denoted $PM_{2.5}$, are called fine particles. The fine particle category typically includes most of the total number of particles and a large fraction of the mass. Fine particles with diameters smaller than 0.1 μm are often called ultrafine particles. Those with diameters less than 10 μm are denoted PM_{10}.

Over the last decade, fine particles ($PM_{2.5}$) have been linked to a range of respiratory and cardiovascular health problems. Effects associated with exposure to ambient particulate matter include premature mortality, aggravation of respiratory and cardiovascular disease, aggravated asthma, and chronic bronchitis. Although these effects have been clearly demonstrated in epidemiological studies, the characteristics of the particulate matter that are responsible for these effects, such as particle size and particle chemical composition, have not been determined. The National Ambient Air Quality Standards for particulate matter, based on human health impacts, are as follows: for $PM_{2.5}$, the three-year average of the 98th percentile of 24-h average concentrations at each population-oriented monitor must not exceed 65 μg m^{-3}, and the three year average of the annual arithmetic mean concentration from single or multiple community-oriented monitors must not exceed 15 μg m^{-3}. For PM_{10}, the fourth highest 24-h concentration over 3 years must not exceed 150 μg m^{-3}, and the three-year average annual mean concentration must not exceed 50 μg m^{-3}. Finally, the nation must improve visibility on the haziest days and ensure no degradation on the clearest days, with the ultimate goal of reaching natural background conditions in 60 years.

A significant fraction of the tropospheric aerosol is anthropogenic in origin. Chemical components of tropospheric aerosols include sulfate, ammonium, nitrate, sodium, chloride, trace metals, carbonaceous material, crustal elements, and water. The carbonaceous fraction of the aerosols consists of both elemental and organic carbon. Elemental carbon, also called black carbon, or soot, is emitted directly into the atmosphere from combustion processes. Organic carbon is emitted directly by sources or can result from atmospheric condensation of low-volatility organic gases.

Particles can be introduced into the atmosphere by two paths: emissions from sources and *in situ* nucleation. New atmospheric particles form from gas-phase reactions by homogeneous nucleation, with sulfate particle formation being the best-known example. Sulfur dioxide, as we have seen, reacts with the hydroxyl radical forming H_2SO_4 vapor as a product. The H_2SO_4 molecules either condense on pre-existing particles or homogeneously nucleate. The condensation path is by far the preferred if sufficient numbers of pre-existing particles are present (Seinfeld and Pandis, 1998). If the quantity of such pre-existing particles is insufficient to accommodate the continuously formed H_2SO_4, its concentration increases to a point where nucleation ensues. Sulfuric acid molecules in the atmosphere always nucleate together with water molecules, and it has been shown theoretically that if ammonia is present, the ternary nucleation of $H_2SO_4/H_2O/NH_3$ is the preferred path (Korhonen et al., 1999). Under favorable conditions (high H_2SO_4 production rate, high relative humidity, low-temperature, low pre-existing PM concentration), tens of thousands of new particles cm^{-3} can be formed in a matter of minutes. Recent data from the EPA Supersite in Pittsburgh (www.epa.gov/ttn/amtic/supersites.html), for which Spyros Pandis, of Carnegie Mellon University and the University of Patras, Greece, is Principal Investigator, show unequivocally ternary $H_2SO_4/H_2O/NH_3$ nucleation as the source of new particles in the northeast U.S. (Gaydos et al., 2004). These particles have diameters of only a few nanometers, and whereas their mass is negligible compared to the rest of the particle distribution, their numbers can easily dominate the total number concentration. Although less is known about this path, organic vapors produced by oxidation of VOCs can also nucleate and form organic particles. These processes have been observed in the laboratory during the oxidation of biogenic hydrocarbons (Griffin et al., 1999), and there is evidence that they also occur near forests (Kavouras et al., 1998).

Coagulation, the collision and adherence of two particles, occurs most efficiently between small (a few nanometers) and large particles (a few micrometers). The rapid Brownian motion of the small particles brings them into contact with the large particles. As a result, coagulation is mainly a process for removing the smaller particles from the atmosphere, with little or no effect on the larger particles. Most particles with diameters smaller than 20 nm disappear after a few hours as they coagulate with larger particles. After a few days, most of the particles with diameters smaller than 0.1 μm also disappear. Coagulation has, for all practical purposes, no effect on the size distribution of particles with diameters above 0.3 μm, which are responsible for most of the $PM_{2.5}$ mass concentration.

Nonprecipitating clouds can affect the aerosol-size distribution through the activation of aerosol as CCN. Aerosol activation (that is, the growth of particles when their critical saturation ratio is less than the ambient saturation ratio of water) depends on the cooling rate and on the number, size distribution, and composition of the particles. Typically (depending on the cloud's maximum supersaturation), particles larger than 0.06-0.16 μm in diameter can be activated to grow to cloud droplets. Upon evaporation of the cloud, a new aerosol spectrum results from the particles formed from the nonvolatile material in the cloud drops. This nucleation scavenging process

Table 2. Time Scales of Tropospheric Processes Involving Particulate Matter (Pandis et al., 1995)

Process	Urban	Remote Marine Boundary Layer	Free Troposphere	Continental Boundary Layer
Transport	2–5 d	1–2 w	3 d–2 w	1–2 w
Condensation	0.01–1 h	1–10 h	2–20 h	0.5–20 h
Coagulation (6 nm)	0.1–1 h	5–15 h	∼1 d	1–3 h
Coagulation (60 nm)	0.1–2 d	10–30 d	∼50 d	1–5 d
Sulfate production (fog)	0.1–1 h	0.01–3 h	N/A	1 h
Sulfate production (cloud)	0.5–5 d	0.01–3 h	N/A	1 h
Sulfate production (gas-phase OH)	0.1–5 d	1–3 w	1–3 w	1–3 w
Dry deposition (∼0.3 μm)	∼1 mo	∼1 mo	N/A	∼1 mo
Dry deposition (<0.03 or >3 μm)	0.5–10 d	0.5–10 d	N/A	0.5–10 d

dominates all other in-cloud scavenging mechanisms for aerosols. As noted earlier, wet and dry deposition are the ultimate paths by which particles are removed from the atmosphere. The typical lifetimes of the submicrometer particles subject only to dry deposition are of the order of a few weeks or longer. Particles with diameters in the 0.1 to 1 μm range have the longest life because of their slow transfer through the quasi-laminar layer next to the ground. For larger particles, the lifetime against dry deposition is of the order of a few days. Large particles (larger than a few micrometers) are collected and removed efficiently by droplets both inside and below clouds. For particles in the 0.5 to 2.5 μm range, nucleation to cloud droplets during the cloud-formation state is the most efficient pathway for their incorporation to cloud, and then rain droplets. Their composition, whether soluble inorganic salts, or slightly soluble organics, or completely insoluble material, is a critical factor for cloud-droplet nucleation and the droplet's subsequent lifetime.

The typical lifetime of particles responsible for most of the $PM_{2.5}$ mass concentration is estimated to be around a week on average. Wet removal of the particles is usually the process that governs these lifetimes. Particles of diameter less than 0.1 μm have shorter lifetimes because of their higher deposition velocities, and also because of coagulation with larger particles. Particles larger than a few micrometers have shorter residence times in the atmosphere as a result of their larger settling velocities and inertia. Table 2 summarizes various timescales of tropospheric processes involving particles.

Volatile Inorganic Atmospheric Particulate Matter. Chemical constituents of aerosols can be classified as nonvolatile or volatile. For example, sodium and sulfate have such low vapor pressures that they can be considered nonvolatile. Ammonia, chloride, nitrate, and water are the main volatile chemical species in atmospheric aerosols. If the relative humidity is sufficiently high, the aerosol inorganics form an aqueous solution. If the relative humidity is sufficiently low, the aerosol inorganics form solid salts, and water may be present only as salt hydrates. For intermediate relative humidities, the aerosol may form an aqueous solution in equilibrium with one or more solid salts.

The presence of inorganic sulfate, nitrate, and ammonium salts in atmospheric aerosols had been established as early as the 1960s. That condensation of gas-phase species was largely responsible for their presence in the aerosol phase was understood; however, the mechanisms that control the abundances of these species were unclear. Stelson et al. (1979) showed that the volatile salt, ammonium nitrate, would partition itself so as to achieve gas-particle phase equilibrium. Once it was recognized that the entire suite of inorganic compounds would be subject to thermodynamic phase equilibrium, models describing that equilibrium rapidly followed (Bassett and Seinfeld, 1983; Stelson et al., 1984), and subsequently by Pilinis and Seinfeld (1987) and Wexler and Seinfeld (1991). These thermodynamic models predict the composition and state of the aerosol as a function of temperature and relative humidity. The phase state of atmospheric particles can be quite complex, including multiple solid phases. Because of the high solute concentrations, especially at lower relative humidities, the aqueous phase is highly nonideal. Moreover, many aerosols exist in a metastable liquid state, supersaturated with respect to dissolved salts. Zhang et al. (2000) compare the most widely used inorganic aerosol equilibrium models. An especially clear description of the theory underlying these models is given by Wexler and Clegg (2002).

Organic Atmospheric Particulate Matter. Particulate carbon has traditionally been divided into three fractions: organic carbon, elemental or black carbon, and carbonate carbon. The latter derives almost exclusively from soil dust. The compounds making up organic carbon vary in volatility, and can exchange with the gas phase in a manner that depends on that compound-dependent volatility. The fact that particulate organic carbon is always an aggregate mix of countless individual compounds that possess a wide range of chemical and thermodynamic properties, makes measurements of particulate organic carbon concentration difficult with any single direct analytical technique.

Organic particulate matter that is formed in the atmosphere when the oxidation products of certain volatile organic compounds condense on pre-existing aerosols is frequently referred to as secondary organic aerosol (SOA). Secondary organic aerosol is formed when VOCs are oxidized in the atmosphere to form higher polarity and, therefore, lower volatility reaction products that then condense and thereby increase the mass concentration of PM (Seinfeld and Pankow, 2003). Because significant secondary organic PM will not condense unless low-vapor pressure products are formed, in general only those parent organic molecules with six or more carbon atoms are capable of producing oxidized products that condense to form SOA. Both anthropogenic and biogenic VOCs can lead to secondary organic aerosol; on a global scale, biogenic VOCs are estimated to be the predominant source (Chung and Seinfeld, 2002), whereas in urban areas anthropogenic VOCs tend to be the dominant source.

The formation of secondary organic aerosol was actually noted by Haagen-Smit in his famous 1952 ozone article. He wrote, "It has been noticed in the fumigation experiments that the vapor phase oxidation of olefins is always accompanied by aerosol formation. . . These effects are especially noticeable with ring compounds having a double bond in the ring, such as cyclohexene, indene, and dicyclopentadiene." (Haagen-Smit, 1952). In commenting on the ubiquity of blue hazes in the atmosphere, Went (1960) concluded that such hazes consist of "very minute, submicroscopic particles." Went proceeded to state that the aerosol formation described by Haagen-Smit could be achieved, not only with a petroleum-based organic, but with biogenic terpenes, such as the pinenes, the molecules that give a pine forest its characteristic smell. Referring back to classic experiments conducted in the 19th Century by John Tyndall of Dublin, Ireland, Went concluded that partial oxidation of these terpenes can lead to condensation of the oxidation products to aerosols.

The formation of secondary organic aerosol was first studied systematically by this author and his group at the California Institute of Technology, beginning in the mid-1980s (See, for example, Odum et al., 1996, 1997). These experiments were carried out in large outdoor (or indoor) transparent chambers, so-called smog chambers (Laboratory chambers are indispensable in the study of gas-phase atmosphere chemistry and atmospheric aerosol formation and growth. Because of the difficulty of isolating chemical and microphysical processes in the atmosphere from the flow and mixing effects, chamber studies provide the means to develop mechanistic understanding of such processes (Cocker et al., 2001)).

Many atmospheric vapor phase organic species, such as those produced by oxidation of parent hydrocarbon molecules, have sufficiently low vapor pressures that they partition between gas and particle phases. The extent of partitioning of any individual organic compound to the aerosol phase depends on the compound's vapor pressure, the nature of the other organic species present, and the amount of liquid water present in the particle. Predicting the atmospheric gas-particle distribution of organic species and water is important in understanding both formation of secondary organic aerosol and the hygroscopic behavior of organic aerosols. Because of a general lack of thermodynamic data for the vast array of organic compounds present in atmospheric aerosols, theoretical estimation techniques are required for compound vapor pressures and liquid-phase activity coefficients.

Once a multicomponent system contains enough condensable material to form aerosol, vapor-liquid equilibrium is governed by

$$p_i = X_i \zeta_i p^o_{L,i}$$

where p_i is the gas-phase partial pressure of species i, X_i is the mole fraction of i in the particle phase, ζ_i is the activity coefficient of species i in the particle phase, and $p^o_{L,i}$ is the compound's vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest. A low value of $\mathrm{p}^{\mathrm{o}}_{\mathrm{L,i}}$ translates into a large value of the gas/particle partition coefficient, X_i/p_i, and, therefore, a high tendency for compound i to be found in the particle phase. The p^o_L values for hydrocarbon photooxidation products span many orders of magnitude, extending down to very low values (for example, 10^{-7} Torr), and it is the low-vapor pressure products that condense most readily to form secondary organic aerosol.

A key phenomenological feature of the behavior of atmospheric aerosols is the uptake of water that occurs as the ambient relative humidity (RH) increases. Although water uptake by inorganic salts is well understood, that by typical organic compounds found in atmospheric aerosols is not (Saxena et al., 1995; Ansari and Pandis, 2000). Such compounds tend to be highly functionalized, for example, acids, diacids, alcohols, carbonyls, and experimental data relating to water uptake for these compounds are not generally available. To predict organic-water interactions, thermodynamic models are required, both for pure compound vapor pressures (most of which are also unmeasured) and liquid-phase activity coefficients, because data are not available for most SOA-relevant compounds.

As an alternative to experimental measurement, computational methods have emerged that seek to predict p^o_L values based on multiparameter structure-based correlations. These include the COSMO method (Klamt and Eckert, 2000; Lin and Sandler, 2002), the method of Makar (2001), and UNIFAC-based approaches, including that of Asher et al. (2002). UNIFAC is among the state-of-the-art methods for estimating activity coefficients for organic species in liquid mixtures, and its development was a watershed in applied thermodynamics (Fredenslund et al., 1975; Sandler, 1999). It is a semiempirical thermodynamic model based on the "solution of groups" approach in which solute and solvent molecules are decomposed into a collection of molecular fragments (Gmehling, 1999). The large set of structural and empirically derived group interaction parameters, derived for both vapor-liquid and liquid-liquid equilibria (Magnussen et al., 1981), available for the UNIFAC model permits the characterization of complex mixtures of nearly all compounds of atmospheric interest (Saxena and Hildemann, 1997) (UNIFAC does not, however, account for interactions between functional groups within the same molecule).

Visibility

Particles suspended in the air interfere with the transmission of light through the atmosphere. The scattering and absorption of light by the particles result in a degradation of visibility, which is manifested as a reduction in the distance to which one can see, and a decrease in the apparent contrast and color of distant objects (Watson, 2002). Increasing concentrations of particulate matter result in roughly proportional increases in the amount of light that is scattered and absorbed by the particles. Increasing relative humidity also increases the amount of light that is scattered relative to that of dry particles because of the uptake of water. In most cases in ambient air, the scattering of light by particles is much greater than the absorption of light by either particles or gases. The combined effect of light scattering and absorption, because of both particles and gases, is called light extinction and is characterized by the extinction coefficient.

The extinction coefficient, denoted b_{ext}, is a measure of the fraction of light that is lost from a beam of light as it traverses a unit distance through a uniform atmosphere. For a beam of light with initial intensity I_{o} after passing through a distance x of atmosphere with extinction coefficient b_{ext} is $I = I_{\mathrm{o}} \exp(-b_{\mathrm{ext}}\, x)$.

The extinction coefficient of particle-free air (the Rayleigh scattering coefficient) at sea level is 0.012 km^{-1} for light at the peak wavelength of human sensitivity. 1.2% of the light in the beam is lost (scattered by air molecules) as the beam passes through one kilometer of a clean atmosphere. For convenience, a megameter, denoted Mm and equal to 1,000 km, is often used as the unit of distance; in this unit the sea level Rayleigh scattering coefficient is 12 Mm^{-1}. The corresponding visual range along a theoretical path that follows the earth's surface would be about 325 km.

The light extinction effects of particles depend on particle size and chemical composition. The particles with the greatest influence on visibility are those of the same size as the wavelengths of visible light (approximately 0.3 to 1 μm in dia.).

Light extinction can be divided into the sum of its scattering and absorption components as follows

$$b_{\text{ext}} = b_{\text{Ray}} + b_{\text{ag}} + b_{\text{sp}} + b_{\text{ap}}$$

where b_{ext} = light extinction coefficient, b_{Ray} = Rayleigh scattering (light scattering by molecules of air), b_{ag} = light absorption because of gases (mainly NO_2), b_{sp} = light scattering by particles, b_{ap} = light absorption by particles. The scattering and absorption by gases (b_{Ray} and b_{ag}) can be calculated knowing the air pressure (altitude) and temperature, and the concentration of NO_2, respectively. To deal with the particle-related extinction (b_{sp} and b_{ap}), a standard approach is to allocate portions of the extinction to each species of the mixture and then sum up the contributions to arrive at the total particle-caused extinction. Although there are theoretical considerations that limit the rigor of such an approach (White, 1986), in practice it has been found useful for estimating the relative contributions of various species to the total light extinction.

With this approach, one sums up the individual contributions

$$b_{\text{sp}} = e_{\text{Sulfate}}[\text{Sulfate}] + e_{\text{Nitrate}}[\text{Nitrate}] + e_{\text{OC}}[\text{Organic Carbon}] + e_{\text{FSoil}}[\text{Soil}] + e_{\text{Coarse}}[\text{Coarse}]$$

and, for absorption of light by particles

$$b_{\text{ap}} = e_{\text{BC}}[\text{Black Carbon}]$$

where the e's are called extinction efficiencies. The units of e are Mm^{-1} per $\mu\text{g m}^{-3}$, hence $\text{m}^2\ \text{g}^{-1}$.

Extinction efficiencies depend on the size distribution and the molecular composition of the sulfates, nitrates, and organic carbon. The extinction efficiencies for hygroscopic substances (sulfate, nitrate, and organic carbon) are dependent on the relative humidity. Values are usually reported for dry particles; the uptake of water can multiply the given sulfate and nitrate efficiencies many fold at high relative humidities. The effect of water uptake on the organic carbon efficiency is not as well established as that for the inorganic salts. Ranges of dry extinction efficiencies used are (Tombach and McDonald, 2003)

$$e_{\text{Sulfate}} = 1.5 \text{ to } 4\ \text{m}^2\ \text{g}^{-1}$$

$$e_{\text{Nitrate}} = 2.5 \text{ to } 3\ \text{m}^2\ \text{g}^{-1}$$

$$e_{\text{OC}} = 1.8 \text{ to } 4.7\ \text{m}^2\ \text{g}^{-1}$$

$$e_{\text{Fsoil}} = 1 \text{ to } 1.25\ \text{m}^2\ \text{g}^{-1}$$

$$e_{\text{Coarse}} = 0.3 \text{ to } 0.6\ \text{m}^2\ \text{g}^{-1}$$

$$e_{\text{BC}} = 8 \text{ to } 12\ \text{m}^2\ \text{g}^{-1}$$

These extinction efficiencies show that the largest visibility benefits per unit change in concentration are gained by reducing sulfates, nitrates, organics, and black carbon. In humid areas the visibility benefit of reducing sulfates and nitrates is further enhanced because of the effect of absorbed moisture.

Nonurban visibility impairment in eastern North America is predominantly a result of sulfate particles, with organic particles generally second in importance. In the West, the contributions of sulfates and organics are comparable, and nitrates play a significant role in the populated areas of California. In some urban areas across North America, black carbon is an important contributor. Soil particles can be important contributors to visibility impairment in areas susceptible to windblown dust.

Visibility in much of the rural United States has generally improved in the past 2 decades, especially in the eastern half of the country. The widespread improvement in visibility reverses a trend of decreasing visibility during the preceding quarter century. The recent visibility improvement that has occurred is associated with a reduction in $PM_{2.5}$ concentrations throughout much of the country. It is largely attributable, in the eastern United States, to a decrease in sulfate-containing particle concentrations as a result of mandated reductions in SO_2 emissions from electric power plants in the mid 1990s.

Receptor Models. Although a great deal of effort has gone into developing and applying atmospheric chemical transport models, which can also be referred to as source-oriented models, a weakness of these models is that their predictions are only as good as the emission inventory that is an input to them. It was recognized that many types of particulate emission sources have a unique set of signature compounds, and that, when detected in the atmosphere, these compounds are essentially fingerprints for that particular emission source. One example is sodium as a tracer for sea salt. If a group of substances are emitted from a source in unique proportions to each other, and if they are not altered chemically in the atmosphere, then this set of substances serves as a fingerprint for that source. If the array of sources in an area can each be characterized by its source signature, then when particulate matter is measured at some location, the contribution of each source to that measurement can be determined by solving a matrix inversion problem. This powerful concept, first introduced by Sheldon Friedlander in 1972 (Miller et al., 1972), and which has come to be called receptor modeling or chemical element balances, has become a standard tool in apportioning sources to ambient particulate matter (Hopke, 1985).

Summary. We largely understand the sources of atmospheric particulate matter and the processes that shape the ambient size and composition.However, the composition and properties of the organic portion of PMA are still not well understood. This is especially true for secondary organic aerosol. A question of both scientific and practical importance is under what conditions new particle formation occurs in the atmosphere. Scientifically, we seek to understand where new particles come from. This issue has practical importance as some physicians have suggested that particle number concentration, not particle mass, may be responsible for the observed health effects of particulate matter. If so, we need to understand the sources of atmospheric particulate number.

Linearity and Nonlinearity

Once the sources of air pollutants are identified, the principal question is - How will reductions in emissions translate into reductions in airborne concentrations? The simplest situation occurs when this relationship is linear, that is, the atmospheric concentration of a species varies in direct proportion to its emissions. Such linearity holds for a chemically inert substance. For example, atmospheric lead levels fell in direct proportion to decreasing lead emissions as lead was phased out as a gasoline additive. However, as we have seen, reactive components seldom behave in a linear fashion. Ozone does not respond linearly to changes in emissions of VOC and NO_x. Changes in NO_x affect gas-phase chemistry and, therefore, change the concentrations of OH, H_2O_2, ozone, and so on. These changes result in corresponding changes in sulfate production rates (both in clean air because of the OH and in clouds because of the H_2O_2).

The situation with particulate matter is even more complex. In short, particulate matter, ozone and other primary and secondary pollutants are related through a complex web of common emissions and precursors, common photochemical production pathways, and meteorological processes (Pandis, 2003). An emission-control strategy that is beneficial to ozone concentrations may be counterproductive for particulate matter concentrations. Moreover, an emission-control strategy that benefits one particulate matter component may adversely affect another. A prime example is sulfate and nitrate.

In the eastern United States, $PM_{2.5}$ is often 50% or more inorganic, and the largest component of the inorganic portion is sulfate. Regulations aimed at reducing $PM_{2.5}$ in this region of the country have focused on SO_2 emission reductions. It has traditionally been assumed that $PM_{2.5}$ levels will decrease linearly as the sulfate concentration is reduced. In the aerosol system of sulfate-nitrate-ammonium-water, sulfate and nitrate compete for the available ammonia. Because ammonia preferentially neutralizes sulfate, the gas-particle partitioning of nitrate is shifted toward the gas phase when the sulfate concentration is high, and toward the aerosol phase when sulfate concentrations are low. Consequently, as SO_2 emissions are reduced and the concentration of sulfate aerosol decreases, some of the vapor phase nitric acid may transfer to the aerosol phase, with the effect that some of the sulfate mass expected to be reduced is replaced with nitrate mass. West et al. (1999) have quantified this nonlinear response for conditions typical of the eastern U.S. and show that, where sulfate reductions induce a significant transfer of nitric acid to the aerosol phase, $PM_{2.5}$ could actually increase as a result. The exact response depends critically on the amount of ammonia in the atmosphere, as well as on temperature and relative humidity. Low-temperature and high RH favor the formation of aerosol ammonium nitrate, with temperature being the more important influence. At sufficiently high temperatures, ammonium nitrate remains in the gas phase, and $PM_{2.5}$ will respond practically linearly to SO_2 reductions.

A useful concept for the design of control strategies for secondary PM is that of a limiting reactant. For cases where such a reactant exists, the secondary PM component responds readily to changes to its concentration whereas at the same time it does not respond to changes in the concentrations of other precursors. This is similar in concept to the NO_x-saturated and NO_x-sensitive regimes in ozone formation. Thermodynamic models of inorganic aerosols can be used to determine if NH_3, H_2SO_4, or HNO_3 is limiting the formation of particulate nitrate, based on measurements of the availability of the gas and condensed-phase concentrations of these precursors (Blanchard et al., 2000).

Some Closing Thoughts

Remarkable advances have been made in reducing air pollution in the United States over the last half century. However, atmospheric pollution still occupies the central focus in global environmental issues, which is not surprising given population growth and associated demands for energy and transportation.

In this review we have not addressed a key area related to air pollution: technological advances in emission control systems and devices. It is such systems that have made air pollution control a reality.

One of the stunning engineering accomplishments in the last half century, and arguably the single most important advance in air pollution control, was the development of the automotive exhaust catalytic converter (Wei, 1975; Shelef and McCabe, 2000; Gandhi et al., 2003). Catalytic converters were first placed in service in 1975 model year vehicles. The requirements of compactness, durability, high volumetric flow rates, and low-back pressure led to adoption of a multchannelled ceramic monolith coated by a high surface area porous layer containing finely dispersed noble metal catalysts. Emissions are controlled by use of a three-way catalyst, coupled with electronic control of the engine's fuel metering system. The three-way catalyst efficiently converts carbon monoxide, hydrocarbons, and oxides of nitrogen to CO_2, H_2O, and N_2 when the engine is operated at or close to the stoichiometric air to fuel ratio. Currently, three-way catalyst formulations containing Pt/Rh, Pt/Pd/Rh, Pd-only, and Pd/Rh combinations are all in commercial use. The three-way catalyst conversion rate depends on its operating temperature, and operating temperatures in the range of 400 to 800°C are optimal for efficiency and catalyst lifetime. Presently, it takes about a minute for the engine's exhaust gas to heat up the converter sufficiently. As a result, a significant amount of the total emissions from a vehicle in a trip are released in the first few minutes of operation. Minimizing emissions during vehicle "start up" remains a key challenge.

A breakthrough in after-treatment of stationary source combustion exhaust for controlling NO_x emissions was the selective catalytic reduction (SCR) process, in which ammonia (NH_3), injected into the flue gas, reacts catalytically with NO_x to produce molecular nitrogen (N_2) and water vapor. In principle, SCR can provide reductions in NO_x emissions approaching 100%. In practice, commercial SCR systems have met control targets of over 90% in many cases. Commonly used catalysts are base metals, which typically contain titanium and vanadium oxides, and which also may contain molybdenum, tungsten, and other elements. SCR technology has been used commercially in Japan since1980, and in Germany since 1986 on power plants burning mainly low-sulfur coal, and in some cases medium-sulfur coal. During the 1990s SCR demonstration and full-scale systems have been installed in US coal-fired power plants burning high-sulfur coal. Their commercial use followed the introduction of stringent limits to regulate NO_x emissions in each country.

There is growing evidence that regional air pollution can contribute to planetary scale changes in atmospheric precursors for ozone formation and particulate matter. The development of Asian economies and the growing use of fossil fuels is leading to significant increases in air pollution in East Asia. Observations over the tropical Pacific Ocean and off the west coast of North America show clear evidence of long-distance transport of pollution plumes from Asia (Newell and Evans, 2000). Effluents from African and South American biomass burning are observed over the tropical Atlantic as well as over the eastern and central South Pacific (see also Wotawa and Trainer, 2000). Saharan mineral dust is routinely observed in Miami. Long-range transport of pollution, especially in the Northern Hemisphere, means that attempts to achieve air quality goals in one region may be compromised by uncontrollable influxes of pollution (Jacob et al., 1999).

In the most extreme case, emissions from beyond the borders of the U.S. may make it more difficult to attain air quality standards in the U.S. This has been noted with respect to ozone levels in California. Transboundary levels of particulate matter tend to be about 1 μg m^{-3} or less and so are not an issue with respect to the PM air quality standards. This is not the case, however, with the new visibility regulation that requires a return to "background" conditions in 60 years. An imported PM concentration of 1 μg m^{-3} can, at levels characterizing background conditions, render the visibility standard very difficult to attain.

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