

## FORMATION AND EFFECTS OF SMOG

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### Summary

This chapter deals with urban air pollution, commonly called smog, and its impacts on ecosystems, agriculture, material substances, and human health. A brief description of the two types of smog (London or sulfurous smog and Los Angeles or photochemical

smog) is presented along with a brief historical perspective. The chemistry of smog is reviewed with a focus on the Los Angeles or photochemical type, which is the dominant type impacting urban, regional, and global environments today. The chemical processes that form photochemical smog from the hydrocarbon and nitrogen oxide emissions of combustion processes are briefly reviewed. The importance of the formation of secondary oxidants (e.g., ozone [O<sub>3</sub>], peroxyacyl nitrates [PANs]) and inorganic acids (sulfuric and nitric) in photochemical smog is stressed. These secondary oxidants and acids play important roles in the effects of smog on ecosystems and human health, as well as in agriculture and materials damage on urban, regional, and global scales. The effects of the air pollutants produced in smog formation are also reviewed. The urban-, regional-, and global-scale impacts discussed include human health effects; damage to buildings, plants, and tree foliage; crop yield reduction; visibility loss; precipitation pollution (acid rain); and radiative balance effects including urban heat islands, weather, and climate. The concept of urban climate impacts is introduced and discussed in light of the radiative properties of the gases and aerosols present in urban atmospheres due to smog formation.

## 1. Introduction

Air pollution observed in many urban areas is commonly referred to as smog. Originally identified with smoke from coal fires mixing with low-lying fogs, the term smog is derived from a combination of the words “smoke” and “fog”. Smog has historically been described as two types named after the places where they were first observed, London and Los Angeles. The London smog has been called reducing or sulfurous smog. This type is identified by high concentrations of sulfur dioxide (SO<sub>2</sub>) and particulate matter. London smog is therefore composed of air pollutants that are emitted directly by combustion processes and are called “primary pollutants”. The most severe episodes of London smog occur in urban areas when low winds and a shallow boundary layer of air act to concentrate the pollutants in a relatively small air volume. The meteorological conditions that enhance this type of smog are usually observed in winter months during the early morning hours. This type of smog, which is characterized by high aerosol loadings and high levels of sulfur dioxide occurs in many cities that are burning coal today. Beijing and Shanghai, China, Cairo, Egypt, Belgrade, Yugoslavia, and Calcutta, India are current examples of urban centers with London type smog.

The Los Angeles smog is an oxidizing smog formed from the photochemical reactions of nitrogen oxides and volatile organic hydrocarbons, which are primary pollutants released from the combustion of fossil fuels in automobiles, power plants, etc. Therefore, the Los Angeles smog, also known as photochemical smog, is identified with high oxidant levels (e.g., ozone) and haze from aerosols formed in the smog chemical reactions. Because these species are created in the atmosphere by photochemical reactions of the primary combustion pollutants, they are called “secondary pollutants”. The Los Angeles type smog is therefore dependent on the daytime intensity of solar radiation, which promotes the formation of the secondary oxidants and aerosols. In contrast to London smog, Los Angeles smog is formed during summer months and later in the day, after the solar radiation has had time to produce the secondary chemical air

pollutants.

The trace gas species formed in photochemical smog include the secondary oxidants ozone, PANs, and inorganic sulfuric and nitric acids. These oxidants and acids play important roles in the effects of smog on agriculture and ecosystems, in human health, and in materials damage on urban, regional, and global scales. Most major cities in the world today suffer from some form of photochemical smog, with some important examples being Mexico City, Mexico, Rio de Janeiro and Sao Paulo, Brazil, Houston, Texas, USA, and Santiago, Chile.

Smog then consists of aerosols and trace gas species that are of concern due to their potential impacts on human health and biota (e.g. agricultural damage, etc.). Both aerosols and trace gas species present in smog are also important in determining the radiative balance of the troposphere, a property known as the greenhouse effect. These species can heat the atmosphere by absorbing infrared and solar radiation, trapping it in the troposphere. Aerosols can also contribute to cooling of the atmosphere, both directly by scattering incoming solar radiation back to space and indirectly by enhancing cloud formation. The net effect of aerosols on the radiative balance of the atmosphere depends on the types of aerosols present, their chemical compositions, and where in the atmosphere they are formed. Thus, the impacts of smog formation on urban, regional, and global scales are a cause for concern with regard to overall ecosystem well-being as well as human health.

## 2. Brief History of Smog

Air pollution has been recognized for some time as an urban problem. Moses Maimonides (1135-1204 A.D.) noted in his writings:

“Comparing the air of cities to the air of deserts and arid lands is like comparing waters that are befouled and turbid to waters that are fine and pure. In the city, because of the height of its buildings, the narrowness of its streets, and all that pours forth from its inhabitants and their superfluities . . . the air becomes stagnant, turbid, thick, misty, and foggy. . . . If there is no choice in this matter, for we have grown up in the cities and have become accustomed to them, you should . . . select from the cities one of open horizons . . . endeavor at least to dwell at the outskirts of the city.”

His description and discussion clearly indicate that in the twelfth century air pollution was already associated with urban environments and their higher population densities. During the fourteenth century, coal burning had become such a problem in London that King Edward I passed a law banning the burning of coal when the English Parliament was in session. This was the first known legislation aimed at reducing air pollution and human exposures to smog.

During the seventeenth century, after the Restoration, John Evelyn, Esquire, was commissioned by King Charles II to write for the crown concerning London's environmental quality and public health status. He wrote *Fumifugium or The Inconveniencie of the Aer and Smoak of London Dissipated* in 1661 A.D. Commenting on the air quality in London due to the combustion of coal, he wrote:

“This horrid Smoake which obscures our Church and makes our Palaces look old, which fouls our Cloth and corrupts the Waters, so as the very Rain, and refreshing Dews which fall in the several seasons, precipitate to impure vapour, which, with its black and tenacious quality, spots and contaminates whatever is exposed to it. . . . It is evident to every one who looks on the yearly Bill of Mortality, that near half the children that are born in London die under two years of age.”

He further noted in his work that a child born in a country village had an even chance of living 40 years. These early works indicated the severity of the problem of air pollution in urban centers, even in pre-industrial times.

In 1775 A.D., English scientist Percival Pott observed that chimney sweeps were at risk to contract cancer due to their professional exposures to coal tars, ash, and combustion products. Thus, the long-term exposure to high levels of coal combustion products was linked to human health as early as the eighteenth century.

## 2.1. London Type Sulfurous Smog

John Evelyn's comments in *Fumifugium* were prophetic. During the continuing expansion of the use of coal and fossil fuels in the nineteenth and twentieth centuries, the air pollution problem continued to increase in major European cities. In London, the smoke that Evelyn referred to in his writings to the King was enhanced by meteorological conditions conducive to fog formation. This combination of smoke and fog led to the commonly used term *smog*. Smog in London and many of the major cities in England during the first part of the twentieth century consisted of high levels of sulfur dioxide mixed with carbonaceous soot and fly ash from coal use in homes and from industrial emissions. The pollutant levels during intense fog conditions led to such serious problems that during the winter of 1952, over 4000 excess deaths were observed due to pulmonary and cardiovascular stress associated with killer smog events. This mortality led to the passage of the British Clean Air Acts of 1956, aimed at reducing the emissions that produce London type smog events.

Europe was not alone in this type of problem. On October 26, 1948, a killer smog event occurred in the United States. In Donora, Pennsylvania, a smog cloud formed, consisting of a poisonous mix of sulfur dioxide ( $\text{SO}_2$ ), carbon monoxide (CO), and metal dust from the smokestacks of the local zinc smelter where most of the town worked. Over the next five days, twenty residents died and 7000 people, half the town's population, were hospitalized with difficulty breathing after being exposed to the cloud. This type of smog is still quite common in many urban centers of the world, particularly in China, India, the Middle East, and Eastern Europe.

## 2.2. Los Angeles Type Photochemical Smog

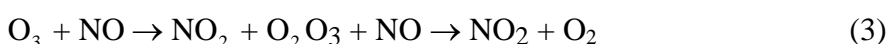
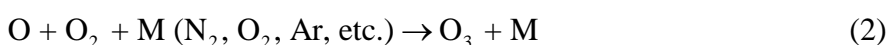
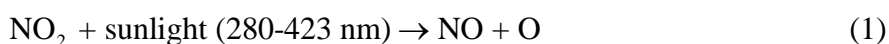
At about the same time that the London smog conditions were being described, a different type of smog was observed in the United States, in Los Angeles, California,

and surrounding areas. This smog was not reducing in nature like the SO<sub>2</sub>-filled smoky air of London. Rather, this was an oxidizing gas cloud filled with nitrogen dioxide (NO<sub>2</sub>), hydrocarbons, and their photochemical product, ozone. The first major photochemical smog event, observed in June of 1943, and was initially thought to be a “gas attack” by the Japanese, as World War II was in full swing. Later, the event was recognized to be a cloud produced by the photochemical reaction of emissions from automobiles and industrial plants in the Los Angeles air basin.

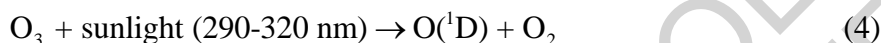
The contributors to photochemical smog are primary pollutants (carbon monoxide and carbonaceous soots, nitrogen oxides, sulfur dioxide, and volatile hydrocarbons) and secondary pollutants formed in the troposphere during photochemical reactions that are driven by sunlight (ozone, PANs, sulfate aerosols, nitrate aerosols, organic aerosols, etc.) (see *Tropospheric Ozone Pollution; Oxidized and Reduced Nitrogen in the Atmosphere ; Gas-Phase (Photo-)Chemical Processes in the Troposphere*). Note that the secondary pollutants formed in photochemical smog are produced at higher concentrations during the summertime because of the higher solar radiation . Atmospheric ozone levels typically reach their highest in the early afternoon due to the sunlight driven chemistry of this type of smog formation. In contrast, the London and Donora type smog events typically occurred during winter periods, when high emissions of the primary pollutants sulfur dioxide and soot combined with low boundary layer inversions leading to high concentrations near the surface. Thus, conditions are typically right for primary pollutant fumigations in the winter and early morning. Similarly, the primary pollutant carbon monoxide has been a major concern in a number of areas during winter months when the emissions from mobile sources and from residential wood burning, together with the lower wintertime boundary layer height, can lead to high levels of this toxic gas in the troposphere. In contrast, the Los Angeles photochemical smog has the highest concentrations of oxidants and secondary pollutants formed during the summertime in the early afternoon.

### 2.2.1. Ozone Formation

Professor Arie Haagen-Smit, a perfumery chemist at the California Institute of Technology, was the first to show that placing automobile emissions containing nitrogen oxides (NO<sub>x</sub>) — consisting of nitrogen oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and unburned hydrocarbons — in sunlight would produce ozone and eye irritants such as formaldehyde. Professor Frances Blacet, chemistry professor at the University of California, Los Angeles, was the first to point out that NO<sub>2</sub> photolysis was responsible for the production of oxygen atoms in the troposphere (see *Oxidized and Reduced Nitrogen in the Atmosphere*). This led to the realization that the following chemistry was responsible for both the production and loss of ozone in the troposphere:



Note that reactions 1-3 lead to a situation where the ozone formation is dependent on the concentration ratio of NO to NO<sub>2</sub> and the sunlight intensity. The observation of elevated levels of ozone in photochemical smog led to the conclusion that other radicals were also important in this chemistry (see *Gas-Phase (Photo-)Chemical Processes in the Troposphere; Tropospheric Ozone Pollution; Oxidized and Reduced Nitrogen in the Atmosphere*). These additional radical species were tied to the organics that were a necessary part of smog formation. A number of researchers concluded that hydroxyl radical (OH), hydroperoxyl radical (HO<sub>2</sub>), and the associated organic peroxy radicals (RO<sub>2</sub>) were key to the photochemical chain reactions that allow for the conversion of NO to NO<sub>2</sub>. Thus, increased NO<sub>2</sub> and decreased NO concentrations result in the enhanced ozone formation due to reactions 1 and 2. The key initiation step leading to the formation of the OH is the photolysis of ozone (O<sub>3</sub>), yielding an electronically excited oxygen atom, O(<sup>1</sup>D), that can react with water vapor (H<sub>2</sub>O) in the air to form the reactive OH species:



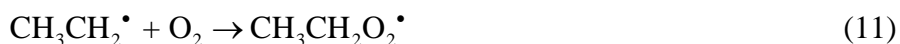
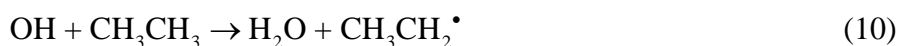
Once formed, OH can react with carbon monoxide (CO) or hydrocarbons to create reactive peroxy radicals and to reform OH, setting up a chain reaction for the production of ozone.

For example, the ozone-producing chain reactions involving CO are as follows:



Reaction 9 provides the starting materials for the formation of ozone via reaction 2. Note that the OH acts to oxidize CO via reaction 6 and is reformed during the oxidation of NO to form NO<sub>2</sub> in reaction 8.

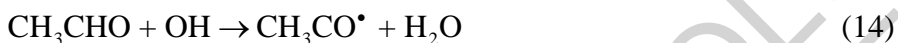
For the case of a simple hydrocarbon, ethane (CH<sub>3</sub>CH<sub>3</sub>), the reaction scheme is:



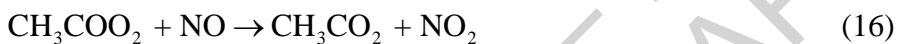
The HO<sub>2</sub> formed from the reaction of the ethoxy radical (CH<sub>3</sub>CH<sub>2</sub>O•) and molecular oxygen (O<sub>2</sub>) can, in turn, react with NO via reaction 8 and reform OH again, initiating a chain reaction. This catalytic cycle will continue until the volatile hydrocarbons are depleted or chain termination reactions occur stopping the chain. The reaction of OH with nitrogen dioxide to form nitric acid is one chain termination reaction that occurs and leads to the formation of acidic species that contribute to aerosol formation (see Section 2.2.3.).

### 2.2.2. Peroxyacetyl Nitrate Formation

Acetaldehyde (CH<sub>3</sub>CHO), emitted directly from automobile exhaust or from secondary reactions similar to reactions 10-13, can also react with OH. The abstraction of the aldehydic hydrogen leads to the formation of an acetyl radical, which can add molecular oxygen (O<sub>2</sub>) to form a peroxyacetyl radical (CH<sub>3</sub>COO<sub>2</sub>):



The peroxyacetyl radical can react with NO to form NO<sub>2</sub>:



This set of smog chemistry reactions leads to the production of formaldehyde (CH<sub>2</sub>O) and the hydroperoxyl radical, which can in turn react with NO to reform OH via reaction 8.

The peroxyacetyl radical also forms a stable adduct with NO<sub>2</sub>, forming peroxyacetyl nitrate (PAN).



Peroxyacetyl nitrate, which is in equilibrium with the peroxyacetyl radical and NO<sub>2</sub>, was initially discovered by agricultural researchers who had identified a new type of plant damage in the Los Angeles air basin. The damage, leaf bronzing of a number of plant species, did not resemble known damage due to ozone, sulfur dioxide, or other air pollutants. The damage, originally attributed to "Compound X", led to studies conducted at the Franklin Institute in Philadelphia and at the University of California, Riverside, where PAN was discovered and isolated and its phytotoxicity was confirmed.

Peroxyacetyl nitrate is not the only compound of this sort, as a number of species of the family of compounds known as the PANs, with the general structure of  $\text{RCO-OO-NO}_2$ , have been found in the troposphere. However, PAN is the most abundant member of this group of compounds. The PANs are eye irritants (i.e., lachrymators). They are not very water soluble, have low photolysis rates, are very slow to react with hydroxyl radical, and are thermally decomposed into their precursors, peroxyacyl radicals and nitrogen dioxide. The PANs are therefore important means of transporting nitrogen dioxide from urban areas on regional and global scales.

### 2.2.3. Aerosol Formation

Over the past fifty years, knowledge of the incredibly complex chemistry involved in the formation of smog has increased significantly (see *Tropospheric Ozone Pollution; Gas-Phase (Photo-)Chemical Processes in the Troposphere*). Besides the oxidants formed from the chemical reactions described in sections above, three other sets of reactions involve chain termination steps. The first of these is the reaction of hydroxyl radical ( $\text{OH}$ ) with nitrogen dioxide ( $\text{NO}_2$ ) to form nitric acid ( $\text{HONO}_2$ ):



Nitric acid formed in this way removes both chain-carrying  $\text{OH}$  and  $\text{NO}_2$ , which forms ozone via photolysis. However, nitric acid is very soluble in water and is a strong acid, and it thus contributes to another aspect of smog — strongly acidic species (see *Acid Deposition*). Nitric acid can also react with ammonia ( $\text{NH}_3$ ) to form ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), an important contributor to secondary aerosol formation in urban and regional settings:



The second reaction involving a chain termination step is the reaction of  $\text{HO}_2$  with itself to form hydrogen peroxide ( $\text{H}_2\text{O}_2$ ):



This reaction removes  $\text{HO}_2$  and therefore is important when  $\text{NO}$  concentrations are lower. Reaction 24 can then compete with reaction 8. Hydrogen peroxide is very soluble in water and can react very rapidly with sulfur dioxide ( $\text{SO}_2$ ) in cloud droplets or on wet aerosol surfaces to form another important strong acid, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (see *Sulfur Dioxide and Sulfur Cycles*):



Sulfuric acid can also react with ammonia to form ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ) and ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ]. Sulfuric acid and the associated ammonium salts are important atmospheric aerosol products. Sulfuric acid is also an important contributor to acidic precipitation.

Larger organic compounds emitted into the air can also be oxidized to form secondary organic aerosols. Indeed, natural monoterpene hydrocarbons emitted from urban trees



can react with the energy-related pollutants and secondary ozone to form a variety of compounds found in smog aerosols (see *Hydrocarbons in the Atmosphere*). Carbonaceous soots can also be emitted directly from automobiles and diesel engines. These soots contain oily organic coatings and associated polycyclic aromatic hydrocarbons (PAHs) and have received some attention as air toxics. Road dusts from tire erosion, road work, and traffic are also a major source of aerosols in many urban areas. Sea-salt aerosols from surf and wind spray can also add to the aerosol burden near ocean shores. Wind blown dusts especially in arid (desert) regions can be important and have been found to travel very large distances including transport across the Atlantic and Pacific Oceans. These windblown dusts are adding to the background in many cities like Beijing, China and contribute to the brown clouds in Asia. All of the aerosol species (organic and inorganic) can play important roles in the radiative balance of the atmosphere on urban, regional, and global scales (see *Greenhouse Gases and Global Warming; Atmospheric Chemistry*).

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### Biographical Sketches

**Jeffrey S. Gaffney** received his Ph.D. in Chemistry at the University of California, Riverside in 1975, under the direction of Professor James N. Pitts, Jr. Since then he has worked at three of the Department of Energy's national laboratories (Brookhaven, Los Alamos, and Argonne) as a principal research investigator in basic and environmental science for the U.S. Department of Energy for over 25 years. He is currently Professor and Chair, Department of Chemistry, University of Arkansas at Little Rock. Dr. Gaffney is also an Adjunct Professor of Earth and Environmental Science at the University of Illinois, Chicago, past Adjunct Research Professor and Faculty Adjunct at the New Mexico Institute of Mining and Technology, and a past Senior Fellow at the Center for Environmental Science (Argonne National Laboratory and University of Chicago). He is the Mentoring Coordinator for the Department of Energy's Office of Biological and Environmental Research's Global Change Education Program. Dr. Gaffney is nationally and internationally known for his work in air pollution and water chemistry, and published over 180 contributions in environmental and basic science. He is particularly well known for his research on peroxyacyl nitrates and aerosols. He is an active member of the American Chemical Society (Environmental and Geochemistry Divisions), the American Meteorological Society, the American Association for Advancement of Science, and the American Geophysical Union. He was awarded the American Chemical Society's Science Policy Award for Outstanding Individual Achievement in Public Policy in 2000.

**Nancy A. Marley** obtained her Ph.D. degree in Analytical Chemistry at the Florida State University in Tallahassee, Florida under the direction of Professor Thomas Vickers in 1984. Before that time she worked for the State of Florida as an Environmental Chemist. In 1989 to 2006, Dr. Marley was research scientist with the Environmental Research Division of Argonne National Laboratory. Dr. Marley is currently Associate Research Professor, Graduate Research Institute, University of Arkansas at Little Rock. She is the Assistant Mentoring Coordinator for the Department of Energy's Global Change Education Program. Dr. Marley is internationally known for her work in environmental science having published over 80 contributions in the areas of analytical and environmental chemistry. She is a past assistant editor of the *Journal of Applied Meteorology* and a member of the American Chemical Society (Analytical Chemistry Division), the American Meteorological Society, the Society for Applied Spectroscopy, and the American Association for Aerosol Research. Dr. Marley is particularly well known for her work in the optical characterization of aerosols and humic and fulvic acids in aqueous systems. Nancy Marley has been a principal investigator on numerous projects for the DOE, NOAA, and other

agencies.

**John E. Frederick** is internationally known for his studies of solar radiation, particularly in the ultraviolet, for approximately 20 years. He received his Ph.D. (Astro-Geophysics) from the University of Colorado in 1975. After two years of postdoctoral work at the University of Michigan, he spent 8 years at NASA/Goddard Space Flight Center working in areas of atmospheric chemical modeling, the calculation of photolysis rates involving complex cross sections for predissociations, and satellite-based remote sensing of the ozone layer using ultraviolet spectroscopy. He joined the faculty of The University of Chicago at the rank of Professor in 1985. In Chicago he has worked primarily in ultraviolet radiative transfer, including modeling and interpretation of measurements from both Antarctica and middle latitudes. Currently he is involved with measurements of ultraviolet radiation in urban areas and how air pollutants affect radiative balance. He has authored or co-authored over 100 papers in refereed journals and has served as a principal investigator or co-investigator on numerous projects supported by NASA, NOAA, EPA, NSF, and private industry. He is currently Professor of Atmospheric Science and Master of Physical Sciences Collegiate Division at The University of Chicago.