

## ENVIRONMENTAL IMPACT OF MOTOR VEHICLES

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### Summary

This article discusses the impacts of motor vehicle emissions on the environment. It begins with a brief introduction to the chemistry of secondary pollution resulting from motor vehicle emissions. The greenhouse gases produced by motor vehicles are then reviewed and related to their potential influence on global climate change. Also presented are some examples of how vehicular emissions and associated smog damage materials and buildings. Vehicle runoff can affect environments surrounding highways, especially water bodies, which is illustrated by a good deal of experimental evidence. Many pollutants produced by motor vehicles, including those produced by the wearing down of

tires and metals, are discussed along with their impacts on ecosystems in general. Lastly, the authors present their personal observations on worldwide environmental concerns of motor vehicle emissions in the past and into the future.

## 1. Introduction

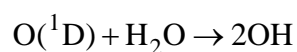
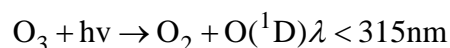
Motor vehicle emissions have a great impact on the environment. This article primarily focuses on the influence of these emissions on ecosystems. Pollutants that are considered include not only emissions from motor vehicle exhaust, fuel evaporation and the resultant secondary pollutants, but also pollution produced by the wearing down of tires and metals. The impacts on the environment including those to buildings, water bodies, and ecosystems will be addressed. Concerns about the effects of vehicle pollution on human health are discussed in *Health Impacts of Motor Vehicles*.

## 2. Impacts of Secondary Pollutants

### 2.1 Photochemical Smog

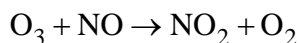
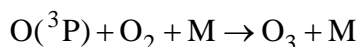
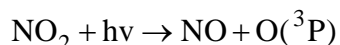
It was in Los Angeles in the 1950s when photochemical smog first came into the public spotlight. This “smog” bore some similarity (but also showed many differences) to winter-time smog, and was observed with growing frequency. The most obvious symptom was visibility degradation; hence the term smog (literally, smoke + fog) was coined. It was found to originate from a series of chemical reactions between  $\text{NO}_x$  and VOCs (volatile organic compounds) in the atmosphere in the presence of intense sunlight. Motor vehicle emissions were identified as the dominant source of emission in most urban areas. The Los Angeles smog, now more generally recognized as a type of photochemical smog, is prevalent in areas with high sunlight intensities and high atmospheric levels of hydrocarbons and oxides of nitrogen. Regions with the most severe photochemical smog problems are the Los Angeles Basin in California, USA, and Mexico City, Mexico. Its presence has also been established in higher latitude regions such as in Western Europe, where most areas may be affected simultaneously during a single tropospheric ozone episode.

The formation process of photochemical smog has two essential starting points: photolysis of ozone and nitrogen dioxide—the former is responsible for formation of hydroxyl radicals and the latter gives rise to a build-up of ozone and other secondary pollutants in the atmosphere. The hydroxyl radical (OH) is a species that is central to many atmospheric chemical reactions. Due to its high reactivity, it is responsible for the breakdown of many pollutant species and consequently to the formation of many secondary pollutants. Ozone photolysis by sunlight ( $h\nu$ ) can lead to the formation of excited-state oxygen atoms, termed  $\text{O}(^1\text{D})$  which then react with water vapor to form hydroxyl, the reactions is as follows:



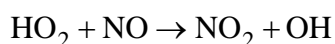
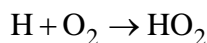
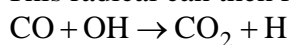
Photolysis of nitrogen directly produces ozone, the other product being nitrogen oxide (or

nitric oxide, NO), which reacts rapidly with ozone to reform nitrogen dioxide, NO<sub>2</sub>:

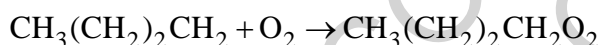
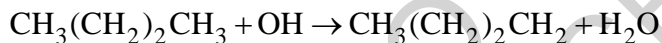


The overall effect of these chain reactions is to form a steady-state ozone concentration.

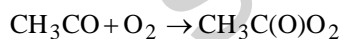
The hydroxyl radical (OH) is also capable of oxidizing CO to CO<sub>2</sub>. The hydrogen atom (H) produced can react with oxygen molecules to form the hydroperoxy radical, HO<sub>2</sub>. This radical can then react with nitrogen oxide.



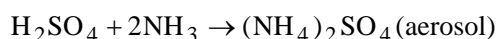
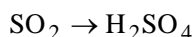
With the participation of hydrocarbons, the photochemical reaction becomes more and more complex. One of their major roles is their contribution to the formation of background ozone in the Northern Hemisphere. An example of hydrocarbon chemistry can be provided using butane, C<sub>4</sub>H<sub>10</sub>; the initial reaction is with OH:



Another important component of photochemical smog is known as PAN. This compound is highly characteristic of atmospheric photochemistry, having no known primary emission source. It has several routes of formation, most notably oxidation of ethanal (acetaldehyde) by the hydroxyl radical:



The production of fine particles within photochemical smog is quite remarkable, they are mainly composed of ammonium sulfate and nitrate produced from primary sulfur dioxide, nitrogen oxides and ammonia. The photochemical “smog” derives its name from visibility-reducing aerosols like these. The main source of ammonia is from animal excrement; in the Los Angeles basin, cattle feed lots are a major ammonia source. Mechanisms of oxidation of SO<sub>2</sub> and NO<sub>2</sub> are described in simple terms as follows:



The ammonium sulfate and nitrate salt compounds are very small in diameter, and such particles scatter light extremely effectively. These particle-forming reactions occur widely in the atmosphere, but are greatly enhanced in photochemical smog by very active photochemical reactions contributing to rapid oxidation of  $\text{SO}_2$  and  $\text{NO}_2$ , giving high concentrations of precursor pollutants. Table 1 shows concentrations of PAN and aerosol in highly and moderately polluted atmospheres.

Pollutant	Concentration (ppb) (1 hour averages)	
	Highly polluted	Moderately polluted
PAN	5 - 35	0.5 - 5
Hydrocarbons (excluding methane)	500 - 1200	50 - 300
Sulfate aerosol ( $\mu\text{g m}^{-3}$ )	10 - 50	5 - 15
Nitrate aerosol ( $\mu\text{g m}^{-3}$ )	10 - 50	5 - 15

Table 1. Concentrations of PAN and aerosols in typical polluted atmospheres

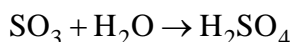
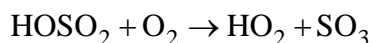
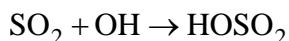
## 2.2 Acid Rain

Acid rain is an important regional environmental problem. Although motor vehicle emissions are not the major cause of acid deposition, their contribution cannot be overlooked. In addition to those aerosols produced in photochemical smog, sulfate and nitrate compounds are formed under other atmospheric conditions and mechanisms and contribute to the production of “acid rain”. Acid rain refers to rainwater and dry deposition with high acidity (low pH value). The most important strong acids in a polluted atmosphere are listed in Table 2.

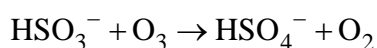
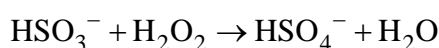
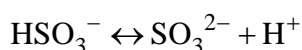
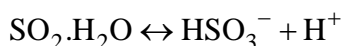
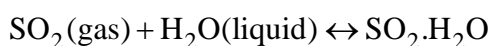
$\text{H}_2\text{SO}_4$	Sulfuric acid
$\text{HNO}_3$	Nitric acid
HCl	Hydrochloric acid

Table 2. Strong acids in the atmosphere

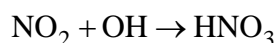
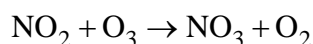
For sulfuric acid, diesel vehicle emissions may be an important contributor, since diesel fuel generally has a relatively high content of sulfur. In dry air, (air without liquid water in the form of clouds or raindrops) the main mechanism of sulfur dioxide oxidation is by reaction with the hydroxyl radical.



If water droplets are available, different mechanisms can function within the aqueous phase.



Formation of nitric acid is more directly associated with roadside pollution with the source being nitrogen dioxide, about half of which comes from motor vehicle emissions in most industrialized countries. For instance, in the United Kingdom, 46% of oxides of nitrogen emissions arise from road traffic. During daytime, nitric acid is formed from the oxidation of  $\text{NO}_2$  by the hydroxyl radical:



The conversion of  $\text{NO}_2$  can proceed at  $\sim 20\% \text{ h}^{-1}$  in bright sunlight in a moderately polluted atmosphere. During the night, a different route for  $\text{HNO}_3$  formation is important, as the concentration of  $\text{OH}$  effectively falls to zero. This involves an initial reaction of  $\text{NO}_2$  with ozone, the resultant  $\text{NO}_3$  radical reacting reversibly with  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$ , which produces nitric acid by reaction with water:



Road vehicles are minor sources of hydrochloric acid emissions. These emissions arise from decomposition of 1,2-dichloroethane that is added to gasoline as a scavenger in alkyl lead additives. As leaded gasoline will be soon phased out worldwide, these will become increasingly less important in the future. The pH of water in equilibrium with atmospheric carbon dioxide is around 5.6, which is weakly acidic. Strong acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  can apparently suppress pH if they are present at considerable concentrations. The actual deposition of acid is the product of hydrogen ion concentration and amount of rainfall. The three best-known acid rain regions in the world are Europe, south-west China, and North America. Among these, south-west China is the only region where sulfuric acid is dominant, due to the large emissions of sulfur dioxide and relatively

low NO<sub>x</sub> emissions in the region.

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### Biographical Sketches

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