



Acid Rain – Not a Basic Problem

An Online Continuing Education Course for Engineers

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Acid Rain – Not a Basic Problem

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Introduction

While air pollution has received a lot of attention in recent years and decades, it is not a new topic or concern for health and environmentally conscious observers. Notable air pollution concerns and effects date back as far as the early 13th century, with more significant attention applied in the 1800s, the peak of the Industrial Revolution. Naturally occurring coal found on beaches and shorelines, known as 'sea coal', gained significant popularity in the Dark and Middle Ages of the British Isles. When lumber demand began to outpace supply, individuals turned to cheap and abundant seal coal to facilitate their home cooking, heating, and manufacturing needs. The heavy, articulate-laden, smoke (smog) created from its use quickly became a notable nuisance in dense population centers such as London, York, and Norwich (historical large cities in England). The problem gained such notoriety that King Edward I banned its use country-wide in 1306, marking the first significant legislation meant to improve air quality.

By the 19th-century, coal use had reentered the lexicon, fueling major advancements during the very prosperous Industrial Revolution. In 1952, a severe smog event in London lasted five days and resulted in approximately 10,000 deaths and 100,000 illnesses. The smog eventually dispersed with weather patterns; however, the harmful effects of air pollution do not end there. The toxic mix of smoke and sulfur dioxide has lasting effects in humans who breath it in, and in the environment where the airborne particulate matter eventually deposits. The toxic mix of smoke and sulfur dioxide, which created corrosive sulfuric acid, paralyzed the city and directly led to the landmark Clean Air Act of 1956.

When the created sulfur dioxide and similar nitrogen-based compounds are pulled from the atmosphere by way of rain (or other precipitation events), the resultant solution is known as acid rain. The acid rain then has deleterious effects on the natural environment, as well as the human populations who rely on its natural resources. While acid rain can be brought on naturally from volcanoes, the adoption of coal-burning facilities, factories, and automobiles has resulted in extensive amounts of acid rain around the world.

Acid Rain (Acid Deposition)

Acid rain is normally defined as the deposition (via precipitation such as rain, snow, sleet, or fog) that has become abnormally acidic due to the presence of sulfur and/or nitrogen compounds in everyday air pollution. These sulfur and nitrogen compounds are most often released by the burning of fossil fuels across a range of industries and applications, and transform to form sulfuric and nitric acids as they enter the environment via dry or wet deposition processes (described in the following sections of this document). While normal rain has a pH around 5.6, acid rain can measure at pH 4 or lower, resulting in

an array of detrimental effects across various aspects of the natural and developed world. Figure 1 depicts the basic formation process of acid rain.

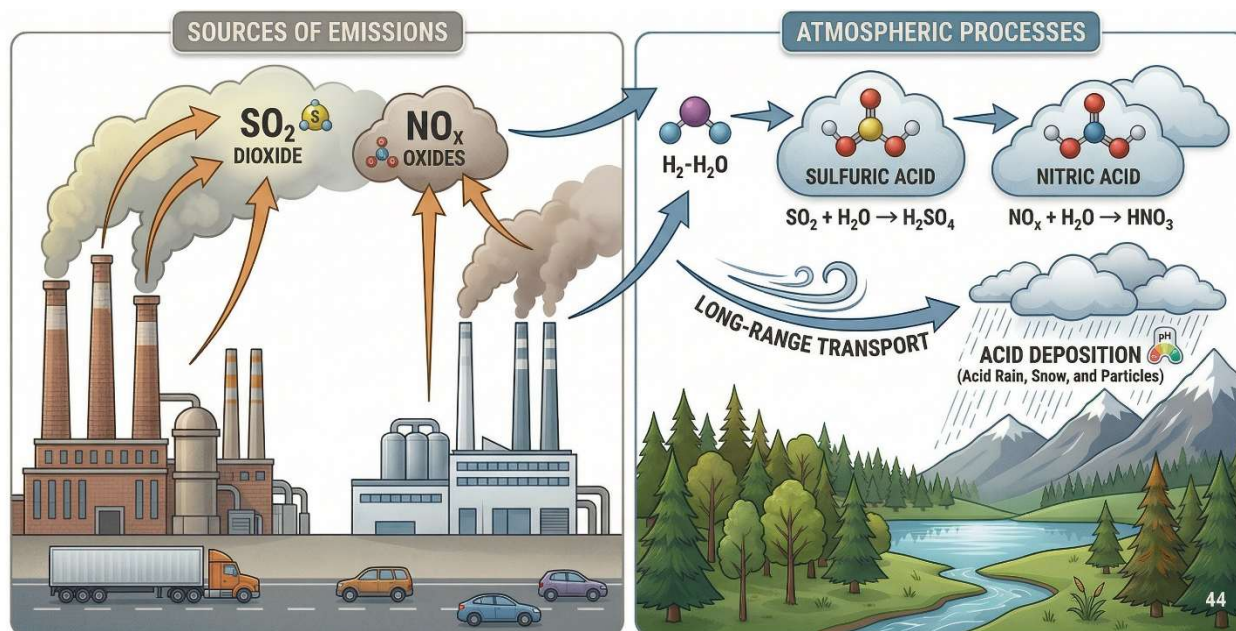


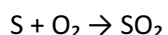
Figure 1. Formation of Acid Rain via Air Pollution

Creation and Transport

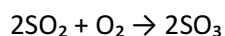
Precursors of acid rain, sulfur dioxide, and various nitrogen oxides can come from a variety of natural and anthropogenic sources. Natural sources, such as volcanic eruptions, decaying vegetation, and lightning strikes, contribute minor, but measurable, amounts of these compounds to the environment. Conversely, anthropogenic sources such as combustion of fossil fuels at power plants, various industrial and chemical processing facilities, and automobile emissions, produce much higher concentrations and total load of these compounds in their respective emissions.

Sulfur

Sulfur, the primary pollutant associated with acid rain, exists in relatively high concentrations in coal and petroleum (crude oil and other processed derivatives). When these sulfur-containing compounds are burned (combusted) for their respective industrial uses, the sulfur undergoes a multistep transformation to create sulfuric acid (H₂SO₄) as indicated by the following chemical reactions.



In combustion, sulfur reacts with oxygen to form sulfur dioxide gas



In the atmosphere, sulfur dioxide gas further oxidizes to sulfur trioxide



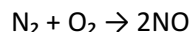
Sulfur trioxide reacts with water vapor to form sulfuric acid and acid rain deposition.

An alternative reaction pathway, and a lesser contributor to acid rain makeup, is the conversion of sulfur dioxide gas (SO_2) directly to sulfurous acid (H_2SO_3). This more direct conversion is typically more prevalent in high humidity (foggy) conditions or at lower temperatures, but it is usually never the predominant transformation. The main types of facilities and industries that rely heavily on sulfur-containing coal and petroleum combustion include;

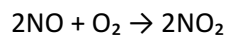
- Power generation
- Steel, cement, paper, and glass manufacturing
- Oil refineries
- Chemical processing facilities
- Locomotives, heavy equipment, ships, marine vessels, and other mobilization equipment
- Some oil-based residential and commercial heating systems.

Nitrogen

Nitric Oxide (NO), the second major contributor to acid rain after sulfur dioxide, forms in similar combustion and transformation processes centered around fossil fuel industries. Additionally, natural gas combustion is a major contributor of nitric oxide to the atmosphere (while having relatively very low sulfur content). When nitrogen-containing coal, petroleum, and natural gas are burned (combusted) for their respective industrial uses, the nitrogen undergoes a multistep transformation to create nitric acid (HNO_3) as indicated by the following chemical reactions.

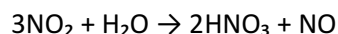


In combustion, nitrogen reacts with oxygen to form nitric oxide gas



In the atmosphere, nitric oxide gas further oxidizes to nitrogen dioxide

Note: Nitrogen dioxide (NO_2) is the reddish-brown gas responsible for the haze over heavily polluted cities.



Nitrogen dioxide reacts with water vapor to form nitric acid and acid rain deposition.

The main types of facilities and industries that rely heavily on nitric oxide-forming combustion of coal, petroleum, and natural gas include;

- Power generation

- Oil refineries
- Chemical processing facilities
- Locomotives, heavy equipment, ships, marine vessels, and other mobilization equipment
- Some oil-based residential and commercial heating systems.
- Waste incineration and municipal, industrial, and agricultural disposal facilities.

Nitric acid typically accounts for about 30% of acid rain acidity, while sulfuric acid accounts for roughly 60-70%. However, in areas with heavy vehicle traffic and lower coal burning, nitric acid can be the dominant contributor.

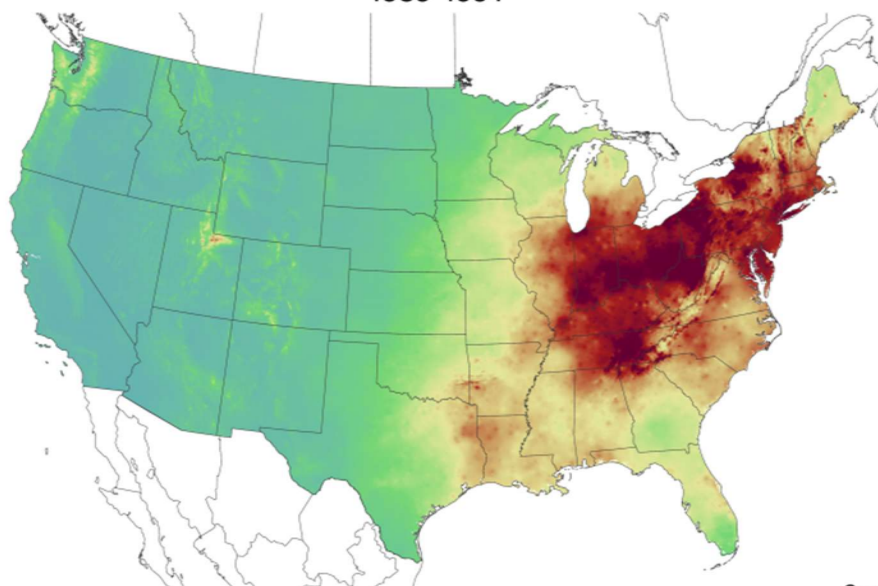
Transport

At the intermediate transformation step, when sulfur dioxide and nitric oxide are present in the atmosphere, is when these air pollutants can travel great distances, leading to transboundary pollution and negative environmental effects. When atmospheric moisture is low, and winds or air currents are high, air pollutants often travel hundreds or thousands of miles to regions and ecosystems that otherwise would not be affected by anthropogenic influences. This dynamic variable often makes air pollution and acid rain not only difficult to contain, but also difficult to forecast for where, when, and how much their effects will be felt.

Numerous different computer modeling software have emerged from a variety of institutions and governments over recent years and decades, each with its own strengths and weaknesses. Some models are best for predicting long-term acid rain deposition and effects, while some are designed for episodic events of bulk acidic pollution events. The Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model, developed within the Environmental Protection Agency (EPA), is one model being used today in the United States. This model assumes a linear relationship between pollutant emissions and depositions, making it best suited for long-term modeling and analysis. The ASTRAP model considers emissions rates, meteorology, diurnal and seasonal cycles, and troposphere seepage to predict the distance and concentration of pollutant transport and dispersion across a given area, making it a viable model to use on a continental or even global scale. While different models analyze data in different ways, each model can provide valuable information that can be thought of as a puzzle piece to the larger picture. By assessing pollutant fate and transport with various models, understanding those models' strengths and weaknesses, a larger understanding of the entire process can be gained, and solutions for remediation and prevention of acid rain can be formulated.

In 1990, the National Acid Precipitation Assessment Program (NAPAP) produced a report that estimated approximately 1/3rd of all sulfur deposition in the northeast United States could be attributed to Midwest coal-burning facilities several hundred miles away, directly due to the prevailing weather patterns in the region. The United States Environmental Protection Agency (U.S. EPA) has conducted air pollution and deposition monitoring throughout its history. Figure 2 depicts annual sulfuric acid (wet sulfate) deposition in the United States during the 3 years between 1989 and 1991.

Annual Wet Sulfate (SO_4^{2-}) Deposition 1989-1991



Source: NADP, PRISM
USEPA, 2024

Figure 2. Sulfuric acid deposition in the United States circa 1990.

There are two main deposition pathways for sulfur dioxide and nitric oxide gases: wet deposition and dry deposition. Wet deposition, the convention form you may think of when thinking about acid rain, occurs with the dissolution of the gases into cloud droplets or precipitation, resulting in acid formation and active transport to ground level. Dry deposition occurs through the gradual settling of airborne particles, via gravity, to any surface (soil, vegetation, water bodies, man-made structures, etc) where they persist until their next rain or moisture event. When the particles, containing sulfur and nitrogen compounds, are mixed with water, the acidic solution then flows through the environment in the same way as typical wet deposition events would. The type of deposition (wet or dry) that predominates an area will be directly associated with the prevailing climate of the region.

The height of the emission source, regional climate and meteorological conditions, seasonal variations, and atmospheric chemistry all influence how far air pollutants can travel and where they ultimately deposit. These dynamic variables often make source attribution of pollution complex and often politically contentious. While emitting regions and receiving regions may share the same federal government, they rarely share the same local government, creating tension between those bearing the economic cost of pollution controls and those bearing the environmental cost of acid depositions.

Environmental and Health Impacts

Acid rain results in a large range of chemical and biological changes in the environment. Acidic additions to surface waters can have harmful, sometimes devastating effects on all species of aquatic life. Acidic

