

## NEW THEORIES TO EXPLAIN ACID PRECIPITATION IN NORTHERN NEW JERSEY

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**ABSTRACT:** *The Northeast Region of the United States is known for its acid precipitation, especially in the New York/New Jersey Metro Region. It has been concluded that nitrogen oxide and sulfur dioxide from auto exhaust emissions and industrial activities have a strong association with the production of acid precipitation in the region. In this paper the author will use two studies of local wet deposition (rain) of the northern region of New Jersey to associate trends between pH levels and landscape and wind direction. The paper makes use of these pH level trends to develop new conceptual models to explain acid deposition: the sea-salt aerosols theory and tree-filter theory. Sea salt aerosols can buffer acid precipitation more so in areas closer to the ocean, in this case, the urban areas of New Jersey. In the forested rural areas of New Jersey, rain falling through and near the leaf canopy can be enhanced before it falls to the ground. Local wind patterns, combined with these buffering factors, can over-ride regional acid precipitation trends.*

### INTRODUCTION

Acid precipitation is a serious problem within urban and suburban regions. This is especially the case in the New York Metropolitan area. New Jersey is one of the states that has the heaviest restrictions on emissions because of the wind transport of air pollution from the Midwest. In previous studies, it was shown that the urban region had pH levels  $>5$  compared to rural areas with pH levels  $< 5$  (Pope et al., 2002). Based on their work, Pope et al. (2002) suggested that higher pH levels near the Metropolitan region may be influenced by ocean waters. It has been suggested that sea-salt removes sulfur from the atmosphere through both buffering and chemical reaction (O'Dowd et al., 1996). This whole process takes place within the boundary layer air circulation.

There are major factors in the transportation of air pollution. Wind speed, wind direction and turbulence are major elements in air circulation that influence air pollution distribution. Weak wind

speeds, such as sea breezes, are associated with high levels of pollution in coastal urban areas (Oke, 1987).

Wind is important to the formation of clouds. About 90% of salt particles that are in the air produce the activation of a cloud base (O'Dowd et al., 1996). This shows that sea-salt is an important element in the formation of a cloud. Particles other than salt, such as ash, city dust, metals, smoke, soil and rock debris larger than  $10\mu\text{m}$  fall quicker to the ground due to Earth's gravitational pull. Particles that are smaller than  $10\mu\text{m}$  remain in the atmosphere and spread throughout the atmosphere (Oke, 1987). While suspended particles, such as sulfur oxide and nitrogen oxide, are in the atmosphere, the particles can undergo chemical and physical transformation (Oke, 1987). These changes vary in temperature, solar radiation, and even atmospheric gases (water vapor, carbon dioxide, ozone, etc).

This paper will explain the basic chemical transformation of sulfur oxide and nitrogen oxide into acid precipitation and using previous studies from Pope et al. (2002) suggest systematic connections between wind direction, cloud formation, and

location of acid precipitation. The author suggests two mechanisms to explain acid precipitation: sea-spray (sea-salt) and tree-filter. The sea-salt theory is an existing theory that is being tested by many researchers. The tree-filter theory is a new theory proposed here by the author. This theory gives new meaning to the importance of trees in the suburban and rural regions of New Jersey. Both mechanisms provide explanations for high pH levels in precipitation in urban compared to lower pH in rural areas.

## METEOROLOGICAL ASPECTS OF AIR POLLUTION

Wind speed and direction are factors in the transport of air pollution within the region (Oke, 1987). On a windy day, air pollution can be transported great distances, but the concentration level of pollution weakens faster with distance (Oke, 1987). High levels of pollution are associated with weak wind speeds, such as sea breezes (Oke, 1987). According to Oke (1987 p.316),

"Local circulation systems (e.g. land and sea breezes, mountain and valley winds and city winds) are not good pollution ventilators for three reasons. First, the speed of these breezes is usually rather low; second, they are closed circulation systems; and third, they exhibit a diurnal reversal in direction of flow".

This statement contradicts the study done by Pope et al. (2002) in Northern New Jersey. The levels of acid precipitation in this study were greater in the western part of New Jersey compared to the eastern part of New Jersey where urban industrial and vehicle traffic are concentrated. But, according to Arya (1998 p.68), "At times, the flow patterns and weather associated with mesoscale systems (sea and land breezes, etc.) may also be beneficial and lead to improved air quality." That means that mesoscale systems may have an effect in ventilating pollution. The direction of the wind is also an important factor, depending on the general aspect and the distance from the pollution source.

Air pollution released into the atmosphere can be transported and diffused at the mixing height in the atmosphere due to air turbulence (Eagleman,

1991). This layer where the mixing takes place is called the boundary layer. Turbulence causes pollutants to mix between a height of 200 m to 1 km with vertical and horizontal motion (Eagleman, 1991). In the mixing of pollutants, the closer to the Earth's surface the weaker the turbulence and wind speed. The mixing height varies throughout the day and year (Arya, 1998): higher during the day and in summer compared to lower at night and in winter. This assumes that the summer atmosphere has a higher pressure, with warm air containing more moisture than cold air, making the mixing height higher (Aguado and Burt, 2001).

## CHEMICAL TRANSFORMATION INTO ACID PRECIPITATION

Three pollutants responsible for lower pH levels in precipitation are carbon dioxide, sulfur dioxide, and nitrogen oxide. Carbon dioxide will be discussed briefly due to its ubiquitous presence in the atmosphere. Sulfur oxide and nitrogen oxide are known as secondary pollutants, because they are formed in the atmosphere through chemical processes (Godish, 1997).

### Carbon Dioxide ( $\text{CO}_2$ )

Carbon dioxide is a nontoxic and major component of photosynthesis. It is a "relatively abundant and variable constituent of the atmosphere" (Godish, 1997 p.32). "Carbon dioxide is produced and emitted naturally to the atmosphere in the biological decomposition, combustion, and weathering of organic matter, and the weathering of carbonates in rock, soil, and water" (Godish, 1997 p.32). Carbon dioxide is removed from the atmosphere by plants and by the earth's crust as coal, oil and natural gas (Godish, 1997). Due to the large combustion of fossil fuels and biomass, the atmospheric levels of carbon dioxide have been increasing and continue to increase.

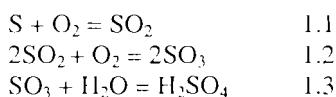
Scientists have estimated that 50% of carbon dioxide emissions produced by humans is removed by the earth's oceans (Godish, 1997). It is also known that plants use carbon dioxide has a source of survival, especially trees. With the removal of

forests, the levels of carbon dioxide will increase. Because CO<sub>2</sub> is ubiquitous in the atmosphere and difficult to trace to point sources, it will not be considered specifically in this paper.

### Sulfur Oxides (SO<sub>x</sub>)

Sulfur oxides are emitted naturally into the atmosphere from sources such as volcanoes, and also by human sources, for example roast sulfide ores and combusted fuel (Godish, 1997). There are five known stages of oxidation of sulfur: hydrogen sulfide (H<sub>2</sub>S), sulfur dioxide (SO<sub>2</sub>), sulfite ion (SO<sub>3</sub><sup>-</sup>), sulfate acid (H<sub>2</sub>SO<sub>4</sub>), and sulfate ion (SO<sub>4</sub><sup>2-</sup>) (Seinfeld, 1998). The primary pollutant that is released into the atmosphere is sulfur dioxide (SO<sub>2</sub>); these are from fossil fuels that contain sulfur, used to produce heat and electrical power (Aguado and Burt, 2001).

The lifetime of SO<sub>2</sub> in the atmosphere can be between two to four days (Godish, 1997). Within that time frame, SO<sub>2</sub> can dissolve into clouds, rainwater, fog and hygroscopic aerosols result in a weak form of sulfurous acid (H<sub>2</sub>SO<sub>4</sub>) (Godish, 1997). Sulfur trioxide (SO<sub>3</sub>) can also be released directly into the atmosphere as a primary pollutant, through oxidation of SO<sub>2</sub> from metal smelting and fossil fuel combustion. As Godish (1997 p.36) states, "because it has a high attractive force for H<sub>2</sub>O, SO<sub>3</sub> converts rapidly into sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)". The equations below summarize the direct oxidation process for SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (Godish, 1997). This explains the transformation from SO<sub>2</sub> to a component that is found in acid precipitation.



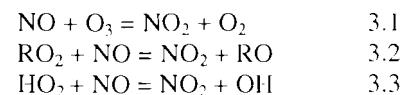
### Nitrogen Oxides (NO<sub>x</sub>)

Nitrogen gas (N<sub>2</sub>) makes up 78% of the atmosphere. There are nitrogen compounds found in the atmosphere in various gas and particle phases: nitrous oxide (N<sub>2</sub>O), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrate radical (NO<sub>3</sub><sup>-</sup>), dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), nitrous acid (HNO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), peroxyacetyl nitrate (CH<sub>3</sub>COO<sub>2</sub>NO<sub>2</sub>), other organic nitrates, ammonia (NH<sub>3</sub>) and hydrogen cyanide (HCN) (Godish, 1997).

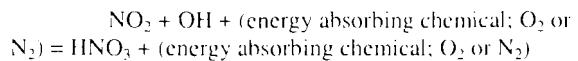
Nitrogen dioxide is a major component of air pollution in an urban region. It can be produced directly through oxidation of NO (Godish, 1997), which is a by-product of high temperature combustion produced by automobiles, industries and electric power generation (Aguado and Burt, 2001).



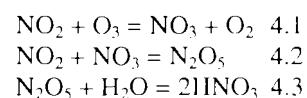
Photochemical reactions involving ozone (O<sub>3</sub>), RO<sub>2</sub> and certain hydrogen species (OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc.) convert NO to NO<sub>2</sub> (Godish, 1997):



Nitrogen falls out of the atmosphere ("sinks") by conversion to nitrous acid. The removal of nitrogen oxides (NO) and nitrogen dioxide (NO<sub>2</sub>) from the atmosphere converts NO to NO<sub>2</sub> and then to HNO<sub>3</sub> (Godish, 1997). This process involves an OII radical reaction with NO<sub>2</sub>



NO<sub>2</sub> can be converted to HNO<sub>3</sub> at night with an ozone reaction and organic compounds such as isoprenes and pinenes (Godish, 1997). Knowing that ozone concentration is lower at night (Duenas et al., 2002), theoretically, this reaction comes about due to the absence of solar radiation:



## REGIONAL ASPECTS OF NORTHERN NEW JERSEY WITH ACID PRECIPITATION

Pope et al.'s (2002) study, "Spatial variability of Acid Precipitation at the Local Scale" sampled precipitation events in order to have a wide sampling area of Northern New Jersey. Table 1 shows the number of sample taken for the event and

## New Theories to Explain Acid Precipitation in Northern New Jersey

**Table 1. Acid precipitation sampling and the statistical trends for pH from Pope et al. 2002**

### **Sampling of Precipitation**

<b>Event</b>	<b>Sample size</b>	<b># of locations</b>	<b>Mean pH</b>	<b>Max pH</b>	<b>Min pH</b>
Rain, Nov. 2, 1999	24	24	$4.84 \pm 0.12$	6.03	4.18
Rain, Feb. 12-14, 2000	35	25	$4.57 \pm 0.12$	6.52	3.86
Snow, Feb 18, 2000	13	8	$5.27 \pm 0.13$	5.74	4.77
Snow, Feb 5, 2001	39	30	$5.30 \pm 0.05$	6.22	4.65

the total number of locations in Northern New Jersey (some locations had more than one sample).

Meteorological conditions from nearby weather stations were also summarized, including, wind direction, lowest barometric pressure, total precipitation and temperature range. In this paper, the author focuses on pH levels and wind direction in three samplings: Nov. 2, 1999, Feb. 12-14, 2000, and Feb. 5, 2001 (Table 2).

#### **Nov. 2, 1999 (Rain)**

This was a relatively warm Nor'easter storm with temperatures ranging from 44.4 – 69.8°F (8 – 21°C). The winds were mainly coming off the Atlantic Ocean onto the New Jersey coastline, as the cyclone center tracked through western New Jersey (Pope et al., 2002). For this rain event, there were a total of 24 samples taken in 24 different locations in Northern New Jersey. Most of the acid precipitation was found in the western part of New Jersey (Pope et al., 2002).

#### **Feb. 12-14, 2000 (Rain)**

This rainstorm tracked through western New Jersey similar to the Nov. 2, 1999 storm but it had cooler temperatures (Pope et al., 2002). The winds were mainly coming from the southwest. For this rain event, there were a total of 35 samples taken in 25 different locations in Northern New Jersey. Most of the acid precipitation was concentrated in Northern New Jersey and mainly found in woodland areas.

#### **Feb. 5, 2001 (Snow)**

This snow event was a cold Nor'easter with temperatures ranging from 32 - 35.6°F (0 - 2°C). As the cyclonic center paralleled the New Jersey coastline it drew winds off the New Jersey shore to the east (Pope et al., 2002). For this event, a total of

39 samples taken in 30 different locations in Northern New Jersey. Most of the acid precipitation was found mainly in areas that contain woodland area, when the urban area had the highest in pH levels

## **THEORIES ON ENHANCING OR BUFFERING ACID DEPOSITION**

### **Sea-Salt Theory**

Sea spray from wind-whipped waves injects aerosol salt into the atmospheric boundary layer. Stronger winds (for instance, from storms) produce more sea spray. Figure 1 illustrates the acid precipitation distribution from November 2, 1999 (Pope et al., 2002) and the wind and topographic features of the region. Aerosol salts would buffer acid precipitation. In the case of the storm of November 2, 1999, onshore winds transported sea salts inland (Figure 2).

The effects of wind on the ocean are supported by O'Dowd et al. (1996). Sea-salt in the air is produced by water vapor from the ocean being blown by the wind. This water vapor can be found around whitecaps on ocean waves where the water is turbulent, dispersing moisture in the air. Wind speed will determine the mass volume of the sea-salt vapors.

Sea salt aerosols are evenly distributed within the marine mixing layer (~400m), according to LIDAR measurements (Rosenfeld, 2002). According to Rosenfeld (2002), a combination of large aerosols size, enhanced drop coalescence, and lower updrafts velocities over water correspond to a greater potential to incorporate salts into precipitation. "Apparently, the height that polluted cloud tops have to exceed to

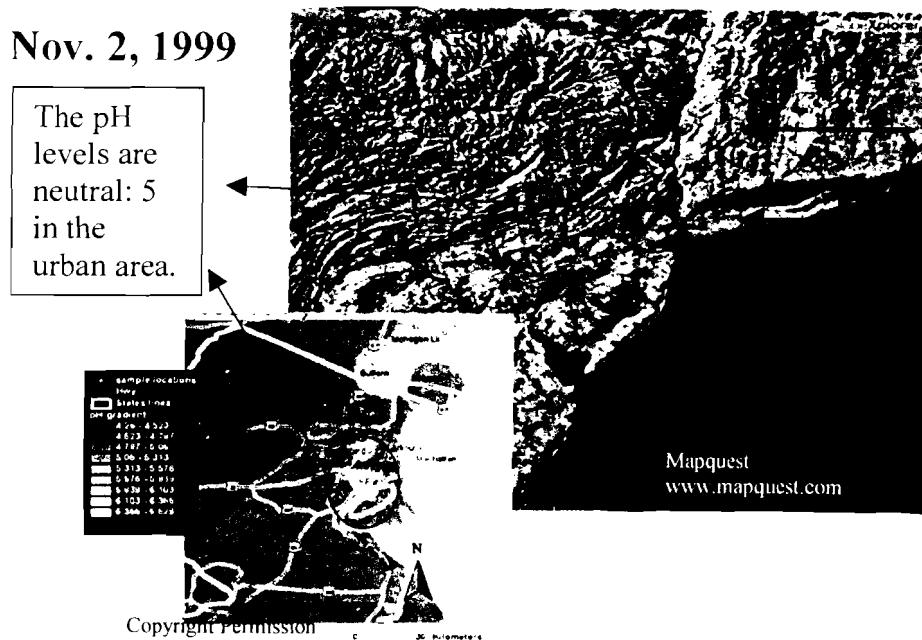


Figure 1. Wind flow, topography, and acid distribution for November 2, 1999 storm.

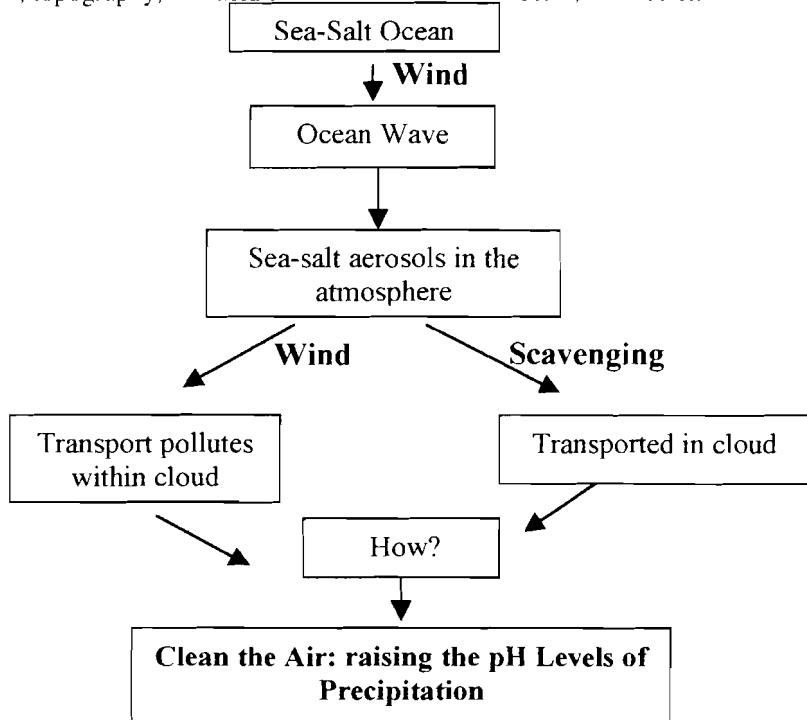


Figure 2. Sea salt buffering interactions.

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Table 2. Summary of meteorological conditions with each precipitation event

Station & Date	Winds	Lowest Barom.	Total Precip.	Temp. Range
<b>Rain, Nov. 2, 1999</b>				
Newark Airport	NE-SE-SE	995 mb	25.3 mm	11 - 19 °C
Caldwell Airport	NE-SE-SE	995 mb	39.4 mm	8-20 °C
Morristown Airport	none-none-SE	N/A	N/A	12 - 20 °C
Teterboro Airport	E-SE-SE	995 mb	25.6 mm	9 - 21 °C
Kennedy Airport	E-ENE-SE	995 mb	19.8 mm	10 - 19 °C
<b>Rain, Feb. 12-14, 2000</b>				
Newark Airport	SSE-none-W	1002 mb	12.4 mm	3 - 10 °C
Caldwell Airport	S-var-WSW	1003 mb	24.3 mm	3-9 °C
Morristown Airport	SSE-none-WSW	1002 mb	N/A	4 - 11 °C
Teterboro Airport	SE-var-WSW	1002 mb	26.1 mm	2 - 9°C
Manhattan	S-var-nonc	1002 mb	12.7 mm	3 - 10 °C
<b>Snow, Feb. 5, 2001</b>				
Newark Airport	NE-NNE-WNW	1005 mb	17.5 mm	1 -2 °C
Caldwell Airport	ENE-N-N	1006 mb	N/A	N/A
Morristown Airport	ENE-N-WNW	1006 mb	N/A	1 -2 °C
Teterboro Airport	NNE-WNW	1004 mb	19.1 mm	0-2 °C
Kennedy Airport	NE-W-W	1003 mb	18.0 mm	0 - 2 °C

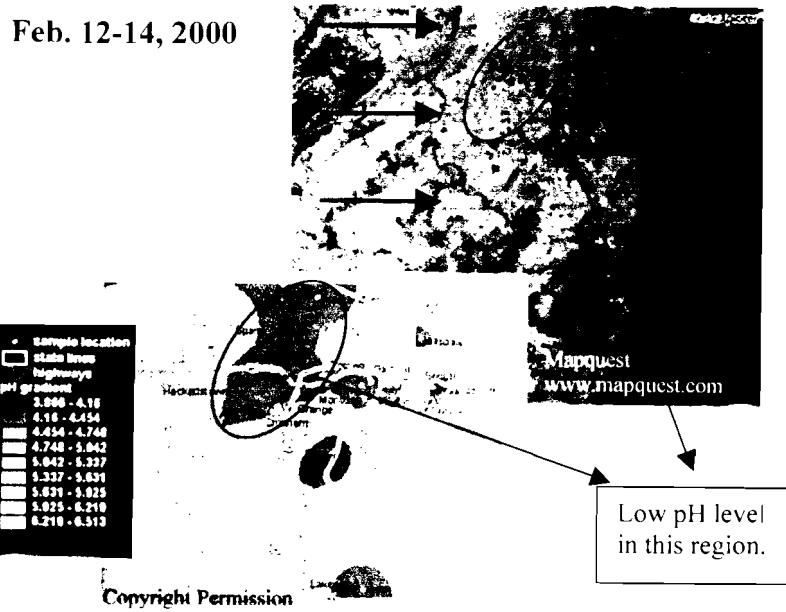


Figure 3. Wind flow, topography, and acid distribution for February 12-14, 2000 storm.

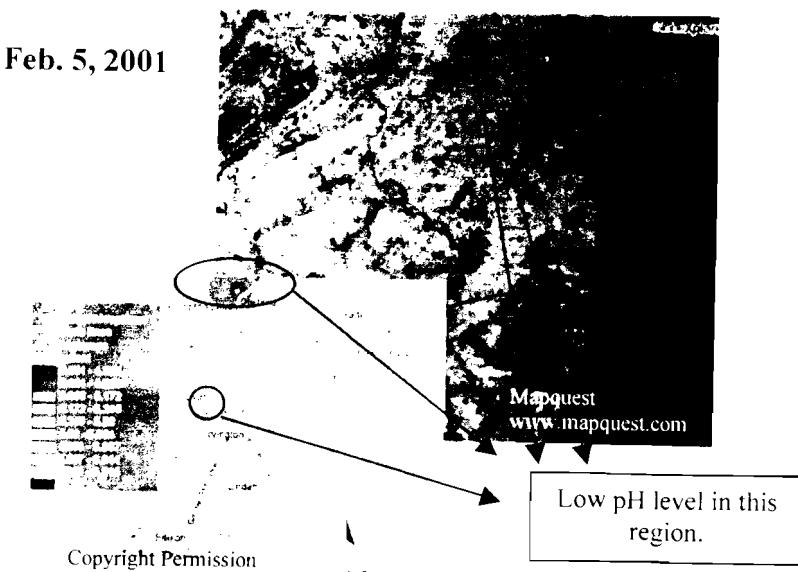


Figure 4. Wind flow, topography, and acid distribution for February 5, 2001 storm.

initiate precipitation is much smaller over the ocean (~3 km or 10 °C isotherm) than over lands" (Rosenfeld, 2002 p.1668). This would have implications for precipitable acids in coastal urban areas.

According to O'Dowd et al. (1996), "activation of aerosol particles within clouds can significantly alter their chemical evolution. The concentration of chemical species, as well as the pH of the faster growing cloud droplets, changes rapidly when activated on entering cloud base". This results in the increase of pH in the cloud droplet, in which "ozone can oxidize SO<sub>2</sub> in a rapid time" (O'Dowd et al., 1996 p.77):

In cloud aqueous phase oxidation of sulfur dioxide to aerosol sulfate occurs in both sulfate-based and sea-salt-based cloud droplets. The production of aerosol sulfate is enhanced in air that contains a significant amount of sea-salt aerosol due to the higher pH associated with newly formed sea-salt-nucleated cloud droplets when compared to those formed on sulfate aerosol.

These mechanisms would appear to be relevant in the buffering of acid precipitation in coastal areas (coinciding with the urban area), regardless of the source of the pollution. The data from November 2, 1999, February 12-14, 2000, and February 5, 2001 storms reported in Pope et al., (2002) support these observations (Figures 3 and 4).

### Tree-Filter Theory

It is believed by the author that trees play a role in low pH levels in elevated and forested regions. Just as trees play along in the highways as a sound barrier, the same can happen to air pollution. As the wind blows, the trees act as a filter, trapping contaminants from the air. This occurs with dry acid aerosols passing through the tree canopy.

The following illustration describes the tree buffering mechanism. Consider two rows of trees (~65-80 ft high), between each row there is a distance of 300 ft. Rain falling through the tree leaves absorbs aerosols that have collected on the leaves and branches; some of these aerosols such as SO<sub>2</sub> or NO increase the acidity. This is similar to aerosol acids that collect on buildings and tombstones (Meierding, 1993). The resulting precipitation reaching the

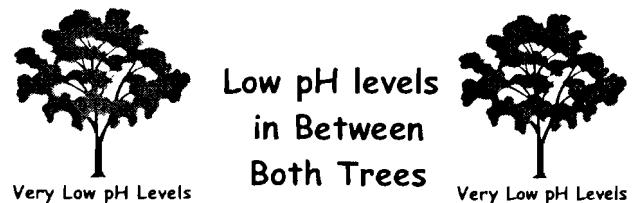


Figure 5. Tree-Filter Theory Illustration.

actually enhance acid precipitation reaching the ground.

Elevation is a secondary factor in the tree-filter theory. As the wind is coming from the west towards Northern New Jersey, the wind comes in contact with mountains and hills. Mountains are more in direct contact with westerly winds carrying regional pollutants (including aerosols blown from Ohio valley, for instance). By this assumption, high elevation with trees have lower pH levels.

## CONCLUSION

The atmosphere contains various types of particles in the air, contributing to the formation of acid precipitation and higher pH aerosols. It was explained that wind contributes to the transportation of pollution great distances, but also as a mechanism to localize and trap pollution. Air turbulence has an influence in the mixing of pollutants in the boundary layer. The three major pollutants of acid precipitation are carbon dioxide, sulfur oxide and nitrogen oxide. Sulfur dioxide and nitrogen oxide are the pollutants of major concern for their concentration in urban areas. It was mentioned that sulfur oxide and nitrogen oxide undergo chemical transformation in the atmosphere in order to become acid precipitation. Previous studies done in the Northern region of New Jersey concluded that there was low pH level of acid precipitation in the high-elevated rural areas compared to low elevation urban region, contrary to what might be expected. The interaction of sea-salts in the coastal boundary layer, and interaction of precipitation falling through leaves in the forested canopy should be considered as modifiers to the precipitation that reaches the ground. Both require further investigation. There is evidence for the removal of sulfur from the atmosphere

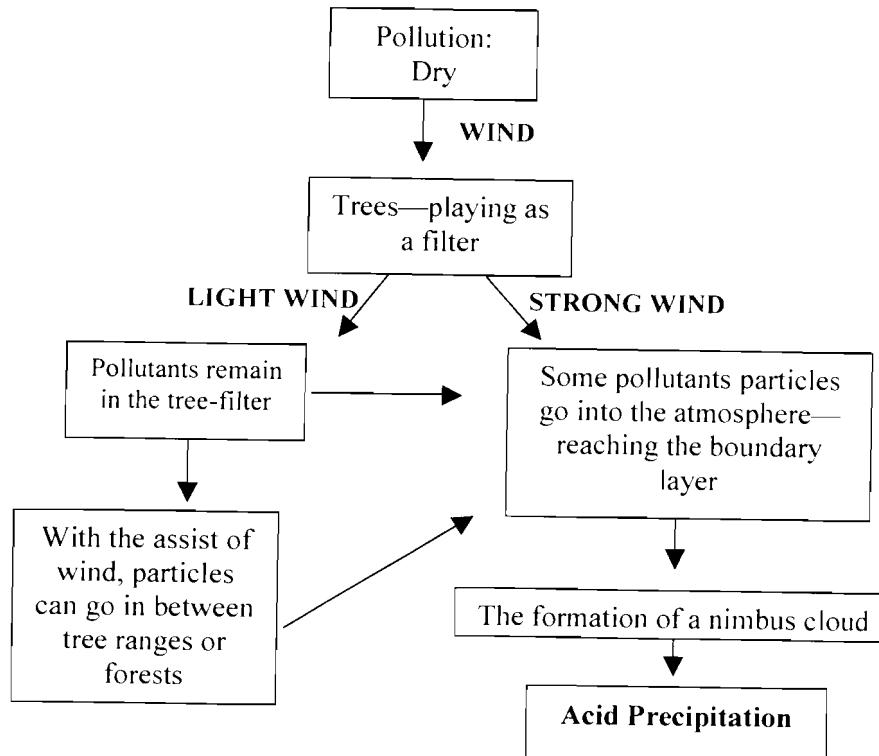


Figure 6. Tree canopy interactions with falling precipitation.

through the interaction of sea salt, though no studies exist yet to explain the removal of nitrogen oxide.

Future studies should test the theories presented in this paper. How can topography, vegetation cover, and ocean influences be used to better predict acid precipitation distribution? What would the impacts be on managing watersheds, protecting ecosystems, and conserving architecture?

Another question for further study concerns the seasonality of pollution and the nature of precipitation. Will the theories proposed here hold up in weather scenarios of different seasons? It has been said by Okay et al. (2001) that emission levels of sulfur oxide and nitrogen oxide are lower during the summer compared to the winter, primarily due to the reduced usage of power plants and fossil fuels. But, with the question of the increased importance of nitrogen oxides, how would summer's increased automobile traffic impact the acid precipitation

environment? Acid precipitation is a complex problem, with many issues yet to resolve.

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