Atmospheric Deposition: Acidity and Nutrients

Background

Atmospheric deposition refers to substances that are deposited on land or water surfaces from the air. These substances can be carried in precipitation, also called wet deposition, or they can reach the earth's surface via dry deposition, which includes both the settling out of particles and the adsorption by soil, trees, water, or other surfaces of gaseous substances.

Rainfall, unless buffered by cations in airborne particles, tends to be naturally acidic, with a pH of about 5.6 due to the formation of carbonic acid from carbon dioxide and oxygen in the atmosphere. However, in much of the eastern U.S., due to anthropogenic emissions of sulfur and nitrogen oxides (SO_x and NO_x, respectively), the concentration of acid in precipitation is so high that the pH of rain is often found to be below 5.6.[1] Most of the SO_x comes from coal-burning power plants, whereas NO_x comes from a variety of combustion sources including power plants, other industrial facilities, area sources (including commercial and residential buildings) and motor vehicles. Emissions of these pollutants can be contributed by sources located in other states upwind of New Jersey.

Deposition of associated nutrients, especially nitrate (NO_3^-) and sulfate (SO_4^{--}), can have important impacts on the environment. Nitrate deposition can increase the potential for eutrophication of coastal and other water bodies and may also cause damage to terrestrial ecosystems, such as forests. Excess nitrate can be harmful to terrestrial ecosystems because it has the potential to harm beneficial fungi[2] and may encourage the growth of invasive species.[3,4,5] Additional sulfate added to the system can combine with calcium and other nutrients necessary for plant growth, causing them to leach more quickly from the soil.

Acid precipitation has damaged wildlife and ecosystems in many areas around the world. Regions where the soils and water bodies have limited buffering capacity, or the ability to neutralize the deposited acids, have been affected the most. The buffering capacity of most soils is sufficient to neutralize naturally occurring acids, but over time the capacity can be overwhelmed by high inputs of acid deposition. A dramatic effect of the acidification of some water bodies is loss of fish species, which has happened in areas such as the Adirondack region of New York State.[6,7]

Ecosystem effects of acid rain are widespread. Studies at Hubbard Brook Experimental Forest in New Hampshire have revealed that concentrations of the

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nutrients calcium and magnesium (which neutralize acidity but are leached from soils in the process) have been lowered and vegetative growth has slowed as a result of decades of acidic precipitation. Studies at other sites in the Northeast also show reductions in nutrient levels as well as the release of aluminum, which can block nutrient uptake by vegetation. Acid fogs and rains also have been found to leach calcium directly from spruce needles, damaging the trees.[8]

Status and Trends

New Jersey has three sites that are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), a nationwide network of precipitation monitoring sites, where acid precipitation and nutrients are measured. The network is a cooperative effort between many different groups, including state agricultural experiment stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities, including DEP. The purpose of the network is to collect data on the chemistry of precipitation for monitoring of geographical and temporal long-term trends. The precipitation at each station is collected weekly and then analyzed at a central laboratory.[9]

Long time series of data on acidity and nutrients in precipitation in the vicinity of the New Jersey area are available for the NADP/NTN sites at Washington's Crossing, NJ, the Edwin B. Forsythe National Wildlife Refuge in Brigantine, NJ, and Milford, PA (just west of northern NJ) (See the Figures 1-3, below). In these charts, parameters that show statistically significant trends are indicated with linear fit lines. Data for the third NADP/NTN station in NJ, Cattus Island, is not presented graphically in this report based on the shorter time series available (2012 to 2019).

For Washington's Crossing, the data show a significant decline in deposition of sulfate, a significant decline in deposition of nitrate, and a significant increase in pH over time (Kendall Tau rank correlation coefficient p values < 0.001). Brigantine and Milford show similar trends, with data from both sites indicating a significant decline in deposition of sulfate, a significant decline in the deposition of nitrate and a significant increase in pH (p values < 0.001). Despite this improvement, the average pH of precipitation in the region remains in the range of 4.9 to 5.2 which is more acidic than expected for unpolluted rain in the Northeast. There are no significant declines in the concentration of the sum of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) ions at any site during the periods sampled.

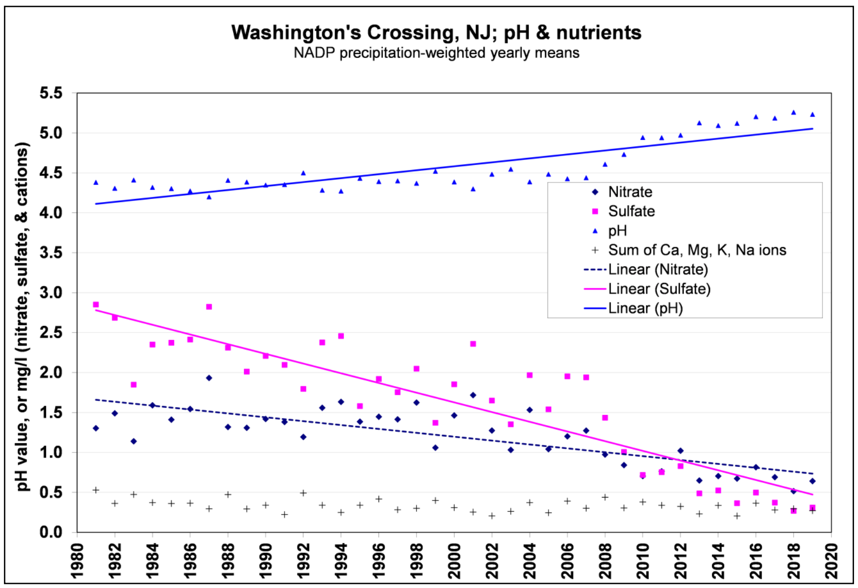

Figure 1. Washington's Crossing, NJ: pH and nutrients deposition.

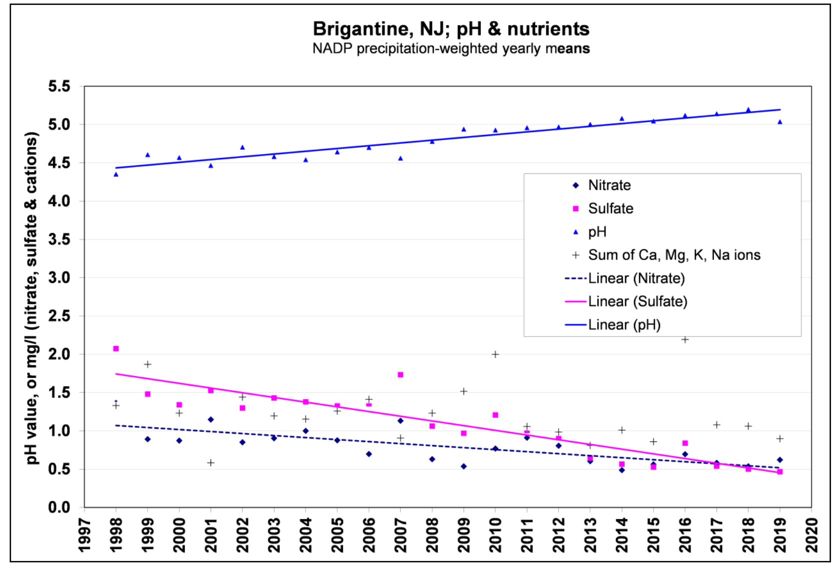

Figure 2. Brigantine, NJ: pH and nutrients deposition.

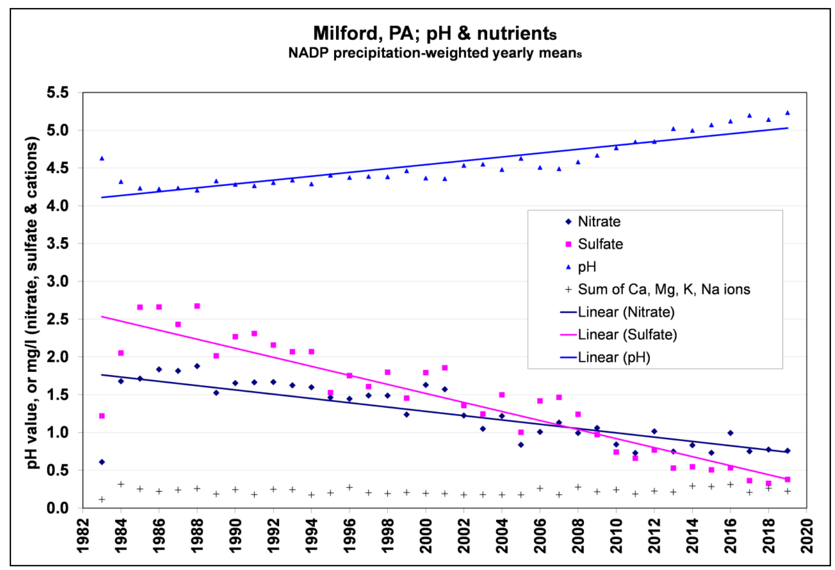

Figure 3. Milford, PA: pH and nutrients deposition.

Reductions of sulfate in precipitation may be related to lower sulfate concentrations observed in some surface waters. A good example is the Pequannock River, near West Milford, NJ. The Pequannock River, upstream of this location, is relatively undisturbed with over 90 percent of the land cover in the watershed as forests, wetlands, or water. Figure 4 shows a significant decline in sulfate concentration over time in that river. The exact portion of the reduction in sulfate due to reduced emissions of SO_2 and NO_x to the air and resulting decreases in acidic deposition cannot be determined as reductions in river concentration may be related in part to changing agricultural practices or other watershed inputs.

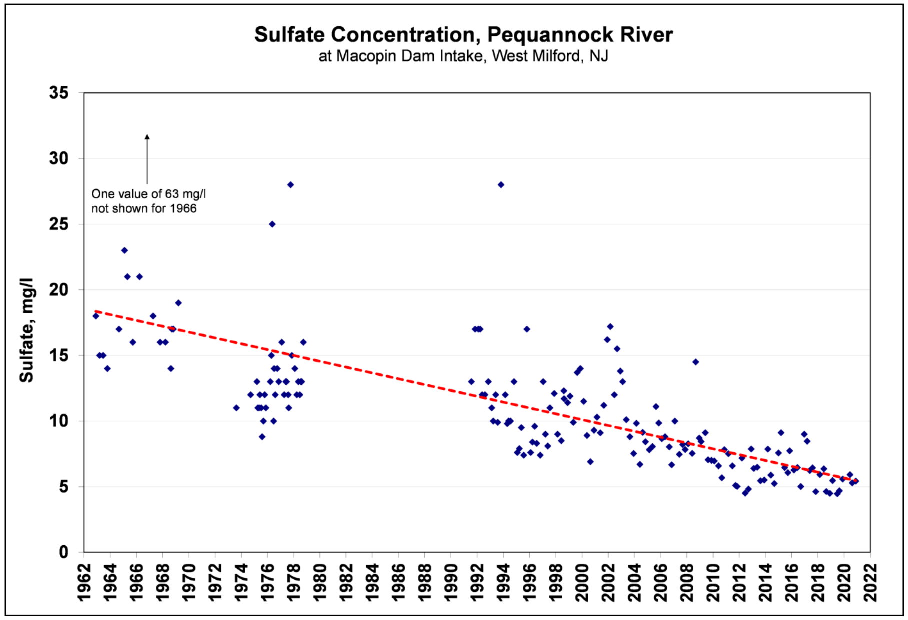

Figure 4. Sulfate concentration in surface water collected by United States Geological Survey (USGS) from the Pequannock River at the Macopin Dam Intake in West Milford, NJ.

Similar reductions in surface water sulfate levels were observed by the U.S. Department of Agriculture in a study of an agriculturally dominated watershed located in east-central Pennsylvania.[10] The USDA found that from 1984 to 2016, atmospheric wet deposition of sulfate decreased 75% (dropping from 10 kg/ha/yr to approximately 2.7 kg/ha/yr) while the concentration of sulfate in the watershed decreased by approximately 30% (from 15 mg/L to approximately 10.5 mg/L). The discrepancy in calculated air deposition and surface water reductions suggests that deposition is not the only contributing source of sulfur. Fertilizers and wastewater discharges are likely other primary sources of sulfate to stream systems.[11,12] Deep well samples collected in 2013 showed evidence of subsurface geology contributing sulfur to the system.

Outlook and Implications

Rules are in place at both the federal and state level to reduce emissions of SO_2 and NO_x from sources such as industrial facilities.[13] Some of these rules have been in effect for three decades and have reduced U.S. emissions of SO_2 by about 93 percent.[14] Studies have shown a virtually universal reduction in deposition of sulfates because of a decrease in SO_2 emissions, but there has not been an equivalent decrease in overall acidity in many regions.[15] For the sites reported here, however, there have been significant declines in acidity (i.e., increases in pH). At Washington Crossing and Milford, pH has risen from approximately 4.3 in the 1980s to greater than 5.0 since 2013. Brigantine has shown a similar degree of improvement. Because pH is a logarithmic scale, these changes represent a reduction of nearly 90 percent in the concentration of hydrogen ions. Despite a general decline in acid deposition in both Europe and North America, some areas show significant delay in aquatic recovery from acidification, and minimal biological recovery in waters or soils.[16] This delay may be due to a depletion of neutralizing substances in soils and water bodies due to years of impact from acidic deposition. Rising levels of atmospheric CO_2 have also been identified as contributing factors of weak acidification in freshwater ecosystems.[17] Continued controls on NO_x emissions at the federal level and in New Jersey are expected to have a positive impact on acidic deposition and nitrate deposition.[18] In addition, a reduced reliance on fossil fuels for energy production is expected to decrease the amount of CO_2 in the atmosphere, which would be expected to help restore the pH of freshwater ecosystems. Whether these reductions will be sufficient to offset long-term impacts on some ecosystems still is unclear.

More Information

DEP Bureau of Air Monitoring website, https://www.nj.gov/dep/airmon/
EPA acid rain program website, https://www.epa.gov/acidrain/acid-rain-program

References

[1] The pH is the antilog of the concentration of hydrogen ions, H^+, in moles per liter. Thus a sample with a pH of 5.0 has 1×10^{-5} moles of H^+ per liter. Rainfall, unless buffered by cations in airborne particles, tends to be naturally acidic, with a pH of about 5.6. This is due to the presence in the air of carbon dioxide, which dissolves in water producing carbonic acid.

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[13] For relevant NJ rules, see http://www.state.nj.us/dep/aqm/rules.html#27. Also see the USEPA acid rain program web site at https://www.epa.gov/acidrain/acid-rain-program.

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[18] Title IV of the Clean Air Act set a goal of reducing annual SO2 emissions by 10 million tons below 1980 levels. This was to be achieved in two phases. Emissions data indicate that 1995 SO2 emissions at regulated units nationwide were reduced by almost 40% below their required level. Phase II, which began in the year 2000, tightened the annual emissions limits imposed on these large, higher emitting plants and also set restrictions on smaller, cleaner plants fired by coal, oil, and gas, encompassing over 2,000 units in all. The Act also called for a 2 million ton reduction in NOx emissions by the year 2000. A significant portion of this reduction has been achieved by coal-fired utility boilers that will be required to install low NOx burner technologies and to meet new emissions standards. See the USEPA acid rain program web site at https://www.epa.gov/acidrain/acid-rain-program and also the NJDEP Air Quality Permitting Program web site at http://www.nj.gov/dep/aqpp/