Notes on pH, the Critical Importance of Buffering, and Acid Precipitation

pH = – log [H⁺]   pH = minus the $\log_{10}$ of the hydrogen ion (H^+) concentration

pH is an exponential (logarithmic or log-base-10 scale) that ranges from 0 to 14 (although 0 and 14 are extremes that usually do not occur).

          Acidic = less than 7   Neutral = 7   Basic = greater than 7

Because it is a $\log_{10}$ scale, for each decrease of 1 pH unit, there is a 10-fold increase in the acidic nature of the water. Example: pH change from 6 to 4 is a 100-fold increase in the acidic nature of the water.
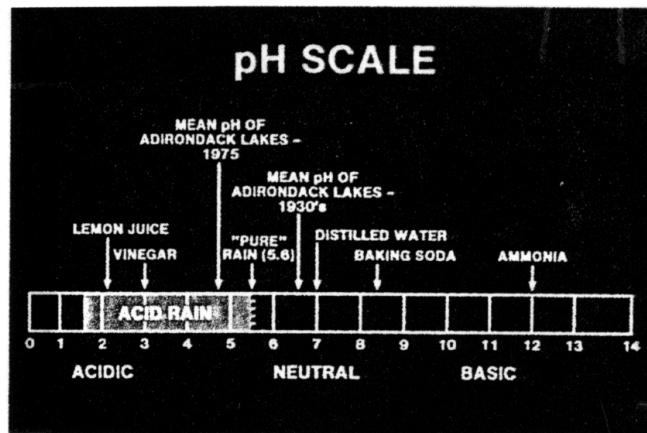

The acidity of substances is measured on the pH scale, wherein each whole number represents a ten-fold increase. Note: The pH of natural rain is 5.6.

pH is regarded as a *master variable* for the chemical state of an aquatic ecosystem because it is a reliable indicator of whether the system is able to protect or *buffer* itself from sudden acidic or basic pollution; and because almost any process (physical, chemical or biological) affects pH either directly or indirectly.

The bicarbonate buffering system

Lakes, streams, and reservoirs are a product of their drainage basin, inseparable from characteristics of their watershed. An important example of this concept is **buffering capacity**. Aquatic ecosystems that lie in basins comprised of carbonate (e.g. limestone regions of the Midwest) are well buffered by the bicarbonate buffering system:

$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$$
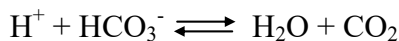
Such **hardwater** systems are neutral to basic (mean annual pH 7.0-8.3), and relatively high in nutrients (N, P) and biological productivity. In contrast, lakes and rivers in igneous rock basins (e.g. granitic material of mountainous coasts) have little buffering capacity. These **softwater**

systems typically are low in dissolved ions (salinity < 1 ppm, dominated by Na^+, Cl^-), mildly acidic (annual pH 5.5-6.5, mean pH < 6.8), and relatively low in nutrients and biological productivity. Softwater habitats are most sensitive to acid deposition.

From Wetzel (2001)
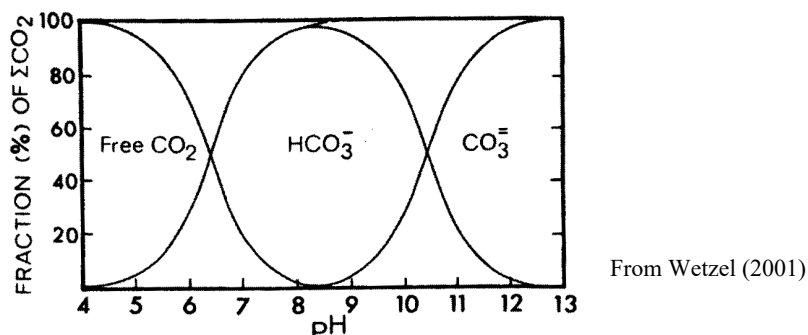
Free carbon dioxide (CO_2, a gas) can be used by all plants for photosynthesis BUT water, unlike air, is very "thick" (viscous) – so carbon dioxide diffuses 10,000 times more slowly through water than through air. This translates into big problems for plants living in the water. There typically is a major struggle to get enough carbon to make a living by photosynthesis. Rapid photosynthesis can quickly remove all of the free CO_2, especially in softwaters. This is usually accompanied by high oxygen production (thus, high levels of dissolved oxygen or DO).

Bicarbonate (HCO_3^-) is abundant in waters that have a pH greater than ~6.8, and some plants can use it as a carbon source for photosynthesis. However, carbonate (CO_3^-) is not used by plants for a carbon source.

Acid precipitation

As emissions of sulfur dioxide and nitric oxide from stationary sources are transported long distances by winds, they form secondary pollutants such as nitrogen dioxide, **nitric acid** vapor, and droplets containing solutions of **sulfuric acid** and sulfate and nitrate that combine with water vapor to form sulfuric acid and nitric acid. Sulfuric acid and nitric acid contribute – 60% and 40%, respectively, of the total acidity of precipitation annually in North America. Because water droplets and most solid particles are removed from the atmosphere fairly quickly, acid deposition is a regional or continental problem. The pH of rain in North Carolina is 4.5 - 4.7 (4.3) (NCSU Atmospheric Impacts Research (A.I.R.) Program).

It is not the average pH value over a season or year that is the "critical limit" for life in an aquatic system. The factor that determines the severity of acidification effects is the lowest pH value that organisms are exposed to during the most sensitive parts of their life cycle – that is, during an **acid spate**.

Stream pH response to acid precipitation. Average rainfall pH 3.6 for the week of Nov. 23-30, 1979; the site was located on Hump Back Creek in the northeastern Great Smoky Mountains National Park, and drains a pre-Cambrian sandstone formation.

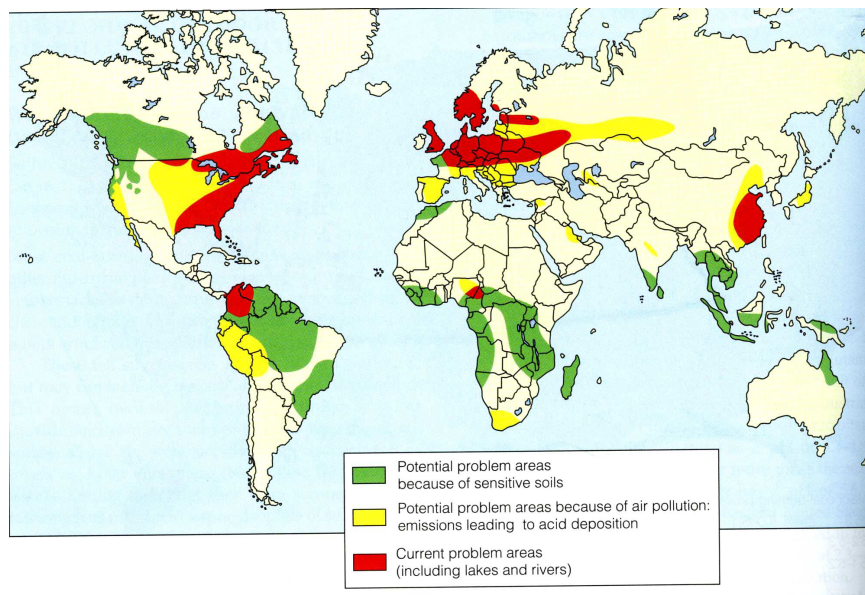During heavy rainfalls, pH can fall by > 0.5 unit wi[...] be
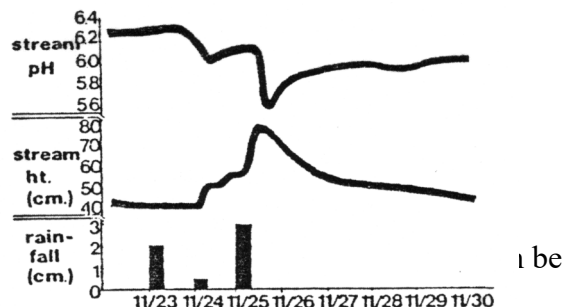
highly damaging to the river ecosystem, but monitoring may be insufficiently frequent to detect them. From rain: Because the first portion of the rain carries a high concentration of acid chemical species into a receiving waterway. From snowmelt: Because there is a fractionation effect, i.e., most of the ionic impurities are carried in the early meltwater.
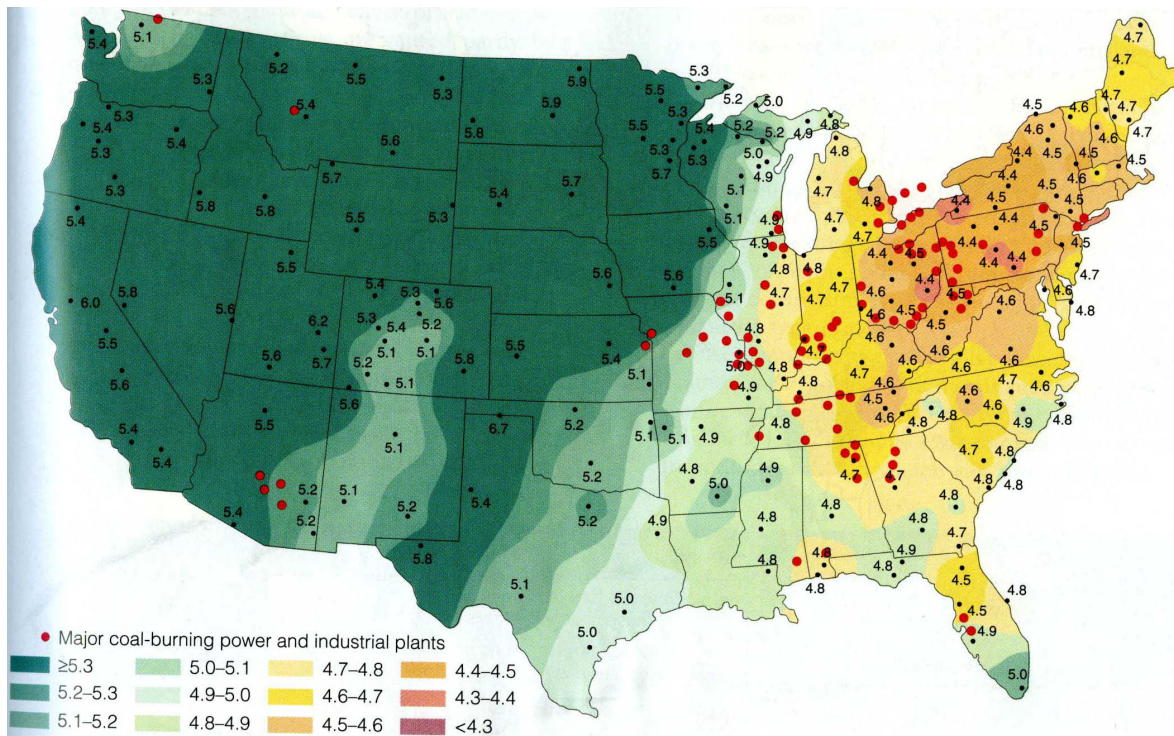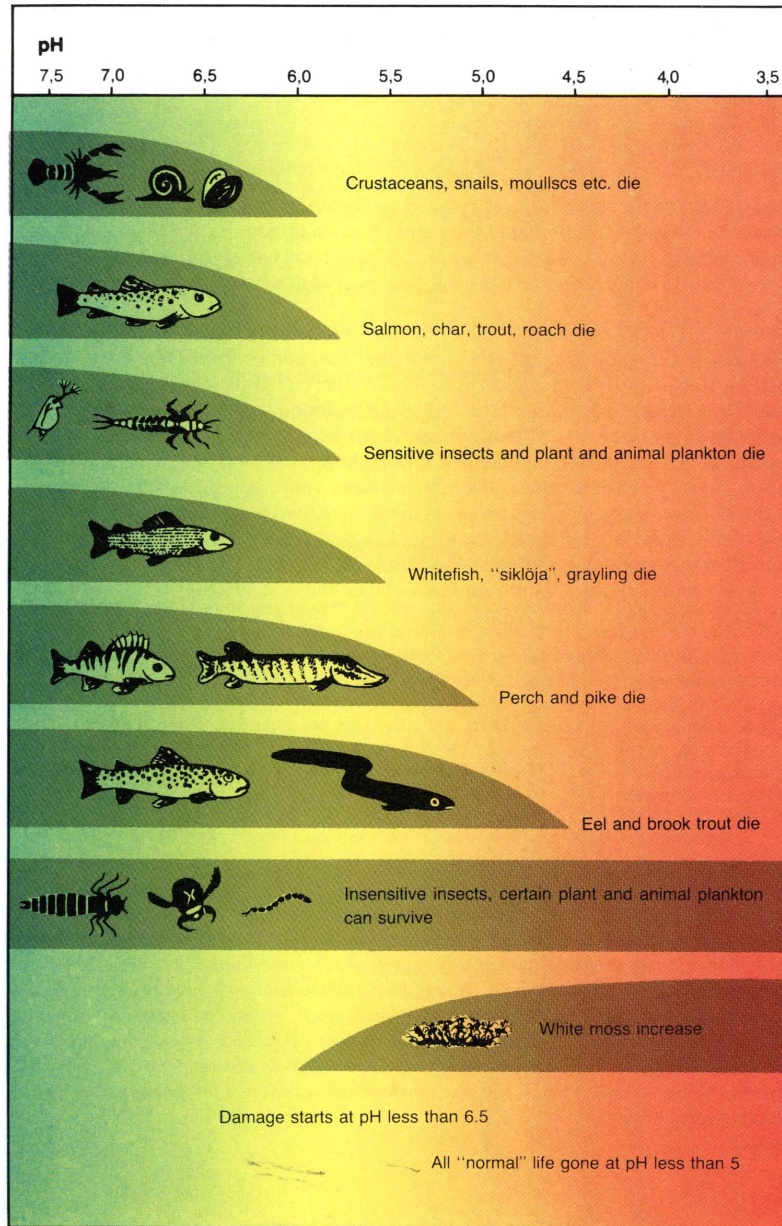

The pH values from field measurements at 250 sites (black dots) in 48 states during 2002. Yellow, tan and rose ≡ areas with lowest pH; red dots ≡ major sources of sulfur dioxide (SO_2) emissions, mostly large coal-burning power plants. The damaging acidic precipitation that falls in the Northeast results from coal-fired power and industrial plants and cars in the region, and pollution that blows in from the industrialized Midwest. In the East the primary component of acid deposition is H_2SO_4 (formed from SO_2 emitted by coal-burning plants). In the West, HNO_3 predominates (formed mostly from NO_x emissions from motor vehicles). EPA: About 2/3 of the SO_2 and ¼ of the NO_x that are the primary causes of deposition come from coal-burning power plants (National Atmospheric Deposition Program / National Trends Network 2003 – in Miller 2005).

Regions where acid deposition is a problem (red) and regions where the potential to develop the problem (yellow, green). Such regions have large inputs of air pollution (mostly from power plants, industrial plants, and ore smelters) or are sensitive areas with soils and bedrock that cannot neutralize acidic inputs of acidic compounds (green areas and most red areas). Sources – World Resources Institute and the U.S. EPA.

The sensitivity of aquatic organisms to a lowered pH in fresh water

pH								
7,5	7,0	6,5	6,0	5,5	5,0	4,5	4,0	3,5

Crustaceans, snails, moullscs etc. die

Salmon, char, trout, roach die

Sensitive insects and plant and animal plankton die

Whitefish, "siklöja", grayling die

Perch and pike die

Eel and brook trout die

Insensitive insects, certain plant and animal plankton can survive

White moss increase

Damage starts at pH less than 6.5

All "normal" life gone at pH less than 5

Acid precipitation causes and aggravates many human respiratory diseases and leads to premature death. Acid deposition is estimated to be the 3rd largest cause of lung disease in the U.S. (after smoking and indoor radon).

Estimated damages from acid deposition already cost the U.S. at least $6 - $10 billion / yr. Costs are expected to rise sharply unless action is taken at this time. In 1990 the research organization, Resources for the Future reported that the benefits of controlling acid deposition will be worth ~$5 billion/yr, ~50% more than the costs of controlling acid deposition.
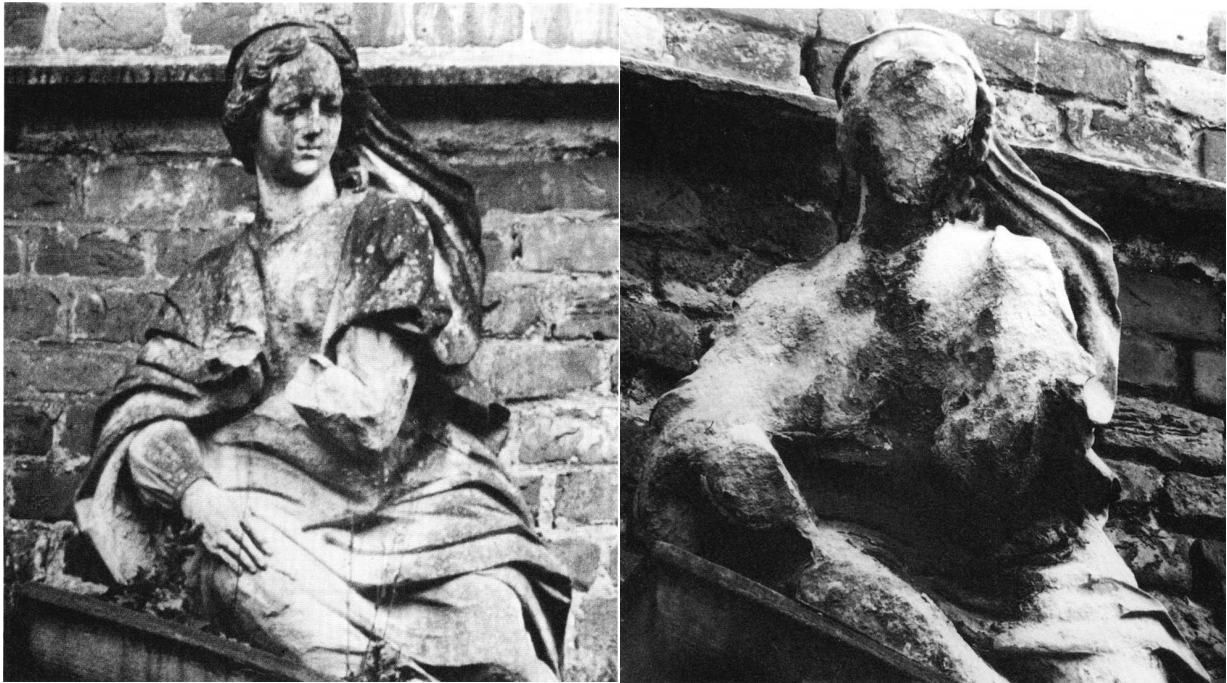
German ornament figure made of sandstone. The figure, made in 1702, is at the Hersten castle in the outskirts of the Ruhr area. The photo on the left shows how the figure still looked in 1908. On the right is the figure 60 years later.

References

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