Lecture 23. Acid rain.

Part2. Effects of acid rain.

Objectives:

1. Alkalinity: The acid buffer.
2. Effects of acid rain.

Readings: Turco: p. 278-284 ; Brimblecombe: p. 178-184

1. Alkalinity: The acid buffer.

Compounds that are basic (alkaline) can act to neutralize acids such as those found in acid rain.

Alkaline compounds which are important in atmospheric chemistry:

ammonium hydroxide (NH_4OH) is a strong base:

formed by dissolving ammonia gas in water

$NH_3(g) + H_2O(l) \rightarrow NH_4OH\ (aq)$

and easily dissociates in the water

$NH_4OH\ (aq) \rightarrow NH_4^+ + OH^-$

sodium hydroxide (or lye) (NaOH) is a strong base:

dissociates in the water

$NaOH\ (aq) \rightarrow Na^+ + OH^-$

calcium hydroxide (or lime) ($Ca(OH)_2$) is a strong base:

dissociates in the water

$Ca(OH)_2\ (aq) \rightarrow Ca^{2+} + 2\ OH^-$

natural alkaline minerals, for instance, **calcium carbonate, $CaCO_3$:**

dissolves in the water

$CaCO_3\ (s) \rightarrow Ca^{2+} + CO_3^{2-}$

then

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$

Buffer solution is one that resists a change in pH when either hydroxide ions or protons are added.

- A buffer solution consists of a weak acid (or base) and a salt of that weak acid (or base) which maintain constant pH despite the addition of small amounts of an acid or base.
- In natural systems, the buffering capacity comes from the minerals in the soils, to varying degrees. Of particular importance are carbonates (CO_3^{2-}), such as limestone ($CaCO_3$).
- How does it work?

$$CaCO_3\,(s) \rightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightarrow \mathbf{HCO_3^-} + \mathbf{OH^-}$$

If protons are added (for instance, from dissociation of an acid)

$$\mathbf{OH^-} + \mathbf{H^+} \rightarrow H_2O$$

If enough protons are added, CO_2 can be released

$$\mathbf{HCO_3^-} + \mathbf{H^+} \rightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2(g)$$

thus added $\mathbf{H^+}$ do not accumulate!

Alkalinity (or acid-neutralizing capacity) is a reservoir of bases in the solution.

For instance, in natural clean waters, most of the acid-neutralizing capacity consists of bicarbonate ion, HCO_3^-. Carbonate alkalinity is defined by

Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

2. **Effects of acid rain:**

a) Acidification of surface waters (lakes, rivers, etc.) and subsequent damage to aquatic ecosystems.

b) Damage to forests and vegetation.

c) Damage of materials and structures.

- Even though the term acid rain implies removal of acidic species from the atmosphere by wet deposition, it is important to keep in mind that the effects attributable to acid rain are in fact a result of the combination of various deposition processes such as dry removal, acid fogs, cloud interception, etc. Historically, this entire process is often called simply acid rain.

- The chemical reactions that change air pollution to acid rain can take from several hours to several days.

How acid rains can damage a lake:

- Acids can cause pH changes of lake's water.
- As the pH of a lake decreases, its chemistry changes and this may have profound effects on the biota inhabiting the lake. For instance, abundant data show a significant correlation between increasing acidity and decreasing fish populations. It is believed that aluminum dissolved from the soil by acid rain is primarily responsible for fish killing.

The interactions between living organisms and the chemistry of their aquatic habitats are **extremely complex**. If the number of one species or group of species changes in response to acidification, then the ecosystem of the entire water body is likely to be affected through the predator-prey relationships of the food web. At first, the effects of acid deposition may be almost imperceptible, but as acidity increases, more and more species of plants and animals decline or disappear.

How it depends on the pH:

pH = 6.0: insects, and some plankton species begin to disappear.

pH = 5.0: major changes in the makeup of the plankton community occur, less desirable species of mosses and plankton may begin to invade, and the progressive loss of some fish populations is likely, with the more highly valued species being generally the least tolerant of acidity.

pH < 5.0: the water is largely devoid of fish, the bottom is covered with undecayed material, and the nearshore areas may be dominated by mosses.

- Terrestrial animals dependent on aquatic ecosystems are also affected. Waterfowl, for example, depend on aquatic organisms for nourishment and nutrients. As these food sources are reduced or eliminated, the quality of habitat declines and the reproductive success of the birds is affected.

How acid rains can damage trees and other plants:

Affect in two ways:

(i) direct deposition of acids causes burning of leaves; alters the protective waxy surface of leaves, lowering disease resistance; may inhibit germination and reproduction; etc.

(ii) acids can alter soil properties in the following ways: react with minerals to leach out some metals, which can be toxic to plants (such as Al, Pb, etc.); change nutrients available to plants; affect decomposition of humus and subsequent organic material, which are necessary for normal plant development.

How acid deposition can affect animal life:

The effects on terrestrial wildlife are hard to assess. As a result of pollution-induced alteration of habitat or food resources, acid deposition may cause population decline through stress (because of decreases in available resources) and lower reproductive success.

How acid rains can damage materials and structure:

(i) Acids can react with limestone ($CaCO_3$) and gypsum ($CaSO_4$) which are often used in buildings and monuments:

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O$$

Thus, acid deposition causes accelerated corrosion, fracturing, and discoloration of buildings, structures, and monuments.

(ii) Acid rain eats away at stone, metal, paint -- almost any material exposed to the weather for a long period of time.

Effects of acid rain on people:

The harm to people from acid rain is not direct. Walking in acid rain, or even swimming in an acid lake, is no more dangerous than walking or swimming in clean water. The air pollution (sulfur dioxide, nitrogen oxides that causes acid rain) is more damaging to human health.

Effects of acid rain on soils:

accelerate leaching of cations and reduce soil fertility.

How it works:

- disintegration and decomposition of the mineral is accelerated by the presence of hydrogen ions, even those associated with weak acid such as carbonic acid.
- the stronger mineral acids in rain water promote weathering (the dissolution of particularly insoluble minerals).

For instance, hydrogen ions in percolation water can replace potassium in mica-related material resulting in the soil itself becoming acidified and soil water becoming enriched in potassium:

mica-K + H^+ -> **mica-H** + K^+

If the amount of H^+ in percolating water increases and remains high, the silicate structure of minerals within soil is gradually destroyed, liberating silicic acid as well as free cations:

$$2KAlSi_3O_8 + 2H_3O^+ + 7H_2O \rightarrow H_4Al_2Si_2O_9 + 2K^+ + 4H_2SiO_4$$

feldspar **kaolinite** **silicic acid**

If soils become very acidic (pH < 3), then aluminum associated with clay minerals may become soluble in the form of Al^{3+} or aluminum hydroxy cations.

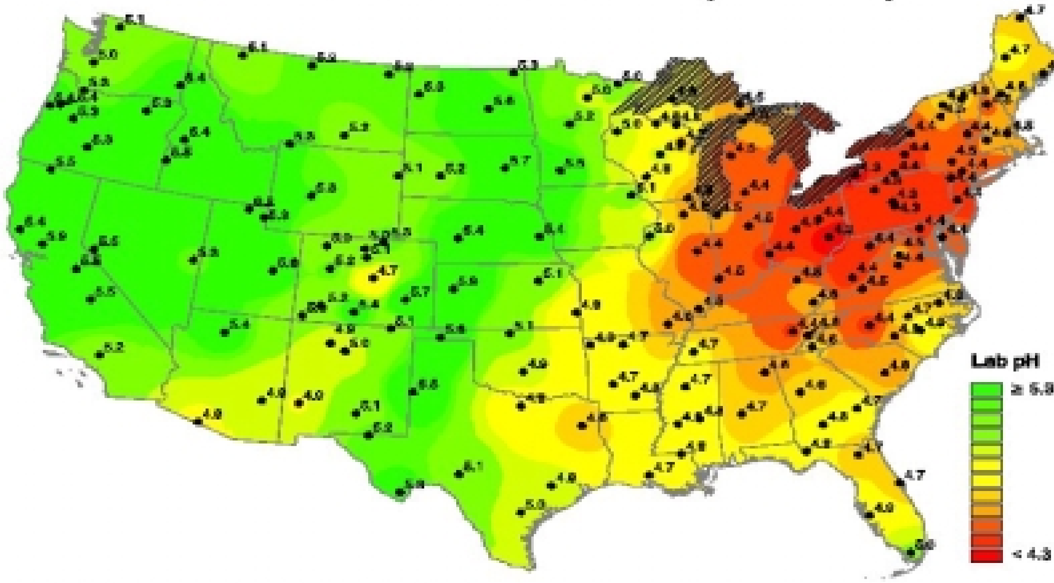
⇒ Soils also have some natural acidity produced by soil microflora and fauna. For instance, coniferous forests can produce an acid litter since the tissues of such vegetation contain considerable concentrations of soluble organic acids.

➢ **Effects of acid rain may differ at different regions** (due to different composition and acidity of rainwater; due to different climatological conditions; etc.)

USA: The northeastern United States, portion of southeastern Canada, and the western coast of United states now receive acidic precipitation.

- In both the western and eastern US, the summer and winter pH spatial patterns are distinctly different. In the eastern US pH (about 4.45 median value) is lower in summer than in winter.
- The center of lowest pH values moves east from NE Ohio to eastern Pennsylvania during summer.
- In the East, summer sulfate rainwater concentration is nearly twice that in the winter, but overall sulfate deposition is just slightly greater in summer. In the western US, summer sulfate deposition is twice that of winter.

Hydrogen ion concentrations as pH for 1996
from measurements made at the Central Analytical Laboratory



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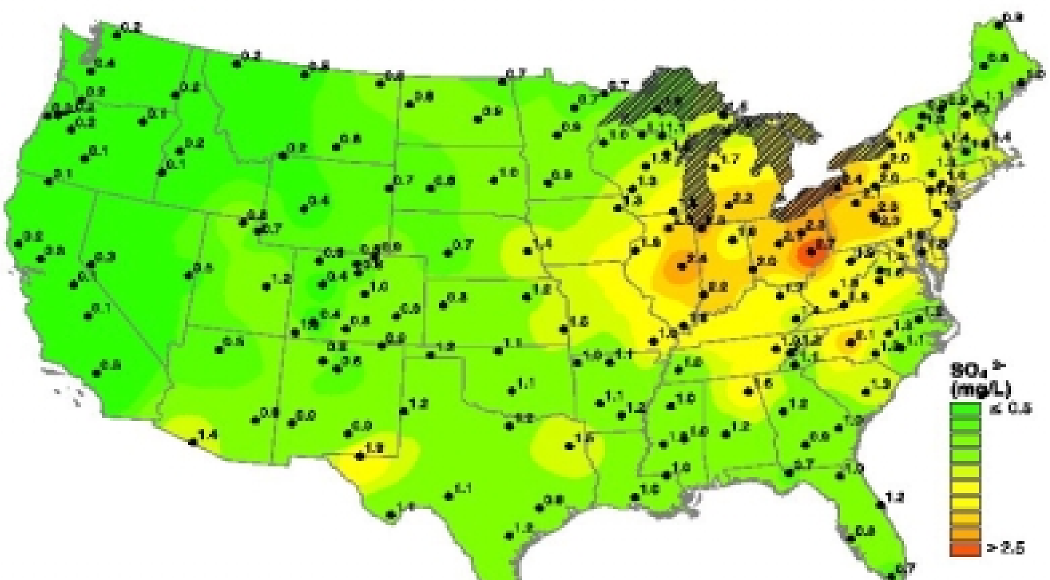
Sulfate ion concentrations for 1996



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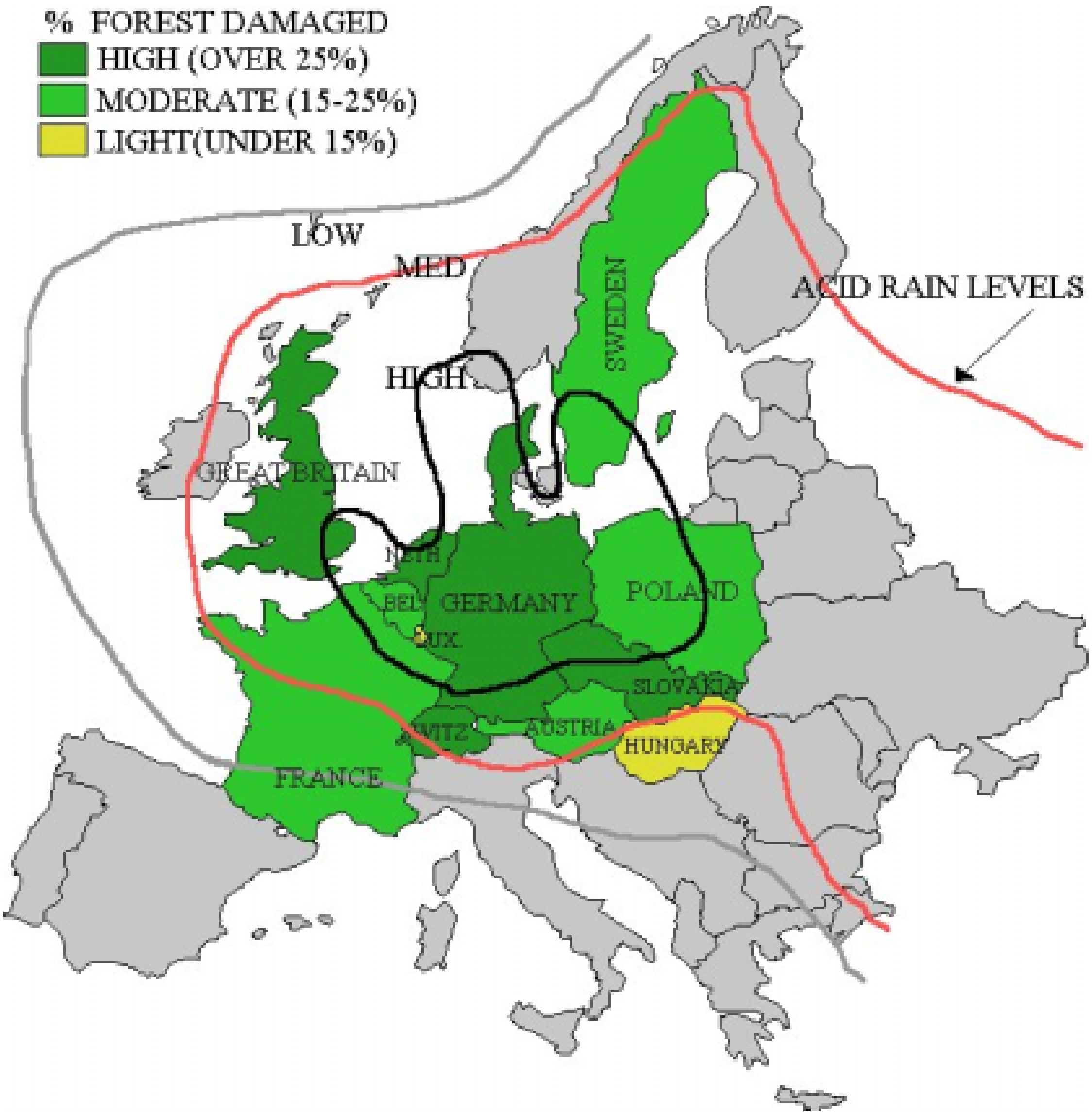
Europe:

- In general, sulfate concentration in precipitation have a maximum in eastern Europe, while the highest concentrations of nitrate in precipitation are found along a line from France to the NE, to the Baltic Sea.
- Significant ammonia deposition is observed in England, Netherlands, and Belgium.
- The pH of precipitation is lowest in southern Scandinavia and in central Europe.
- For the most part, European precipitation and sulfate averages showed sharp declines by the mid-1980s.



China:

there is not enough data to characterize acid rain problem over China.

- About 73% of energy for the country comes from burning coal which is generally of poor quality, with a high sulfur content (3-5%), and the result is high SO_4^{2-}.
- The levels of NO_3^- are low, however, mainly due to the lack of automobile traffic.
- To some extent, acidity of rainwater in China is neutralized mainly by Ca^{2+} from calcareous soil aerosols created by agricultural activities and dust storms.