Lectures 18-19

Rain Acidity

Please read Berner and Berner ("BB") Chap 3 (p62-86 & p116-119)
and Turco Chap 9 (acid rain)

Today and next time

Acid sources to the atmosphere and acid rain (natural and anthropogenic).

- Atmospheric Sulfur Cycle
- Atmospheric Nitrogen Oxide Cycle

Acid rain impacts.

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pH - *natural sources*

pH affects a range of chemical reactions and how dissolved constituents are generated from solids.

pH in natural rain water is <u>largely governed by CO_2</u> from the atmosphere (evenly distributed throughout the troposhere), which sets the <u>pH at ~ 5.5</u>.

► The H_2CO_3 (carbonic acid) system commonly keeps rain buffered between <u>4.3 and 6.5</u>

In rare occurrences "natural" rain can have:
pH>7 - or - pH <4.3.

pH - *natural sources*

Whenever pH < 4.3 (the lower carbonic acid system endpoint) it indicates addition of a strong "mineral" acid, giving rise to the term **"acid rain"**

These include the *Gaseous* mineral acids SO_2 and NO_2.

Other natural chemicals that can affect rain pH are particulate $CaCO_3$ and gaseous NH_3 (both bases raise pH).

pH - *natural sources*

Most aquatic organisms, soil dwelling microbes, land plants and animals *have evolved in systems of limited pH variability* due to the aforementioned natural controls on rain acidity, with *limited ability to regulate internal pH*.

Many complex organisms have internal fluid pH (over most of their bodies) that is buffered at or near the CO_2/H_2O equilibrium value.

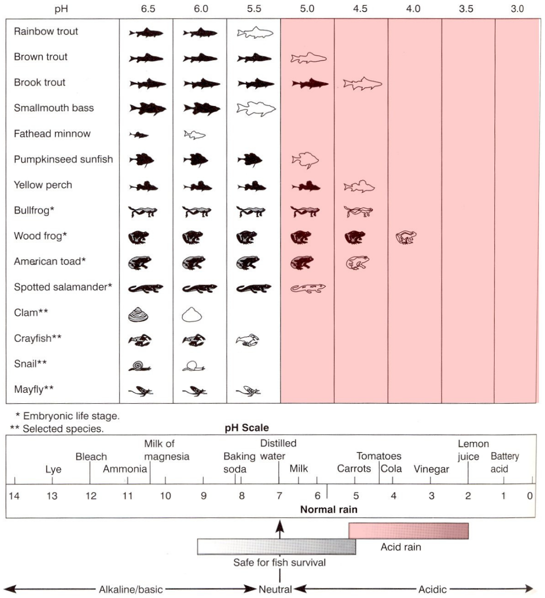


FIGURE 9.6
The effect of pH change on some organisms. The pH scale, the pH range of water considered safe for fish to survive, and the pH range of acid rain are shown for comparison. The approximate pH at which an organism dies with extended exposure to a water with this pH is shown by an organism pattern in white.
(After Christensen, 1991.)

Mackenzie and Mackenzie, "Our Changing Planet"

Acid rain has lowered the pH of many rivers and lakes in affected areas,

with the attendant negative impacts for aquatic flora and fauna.

Note decreasing pH to the right in this diagram

Acid Rain:

Humans have loaded of the atmosphere with acidic N and S oxides (and to a lesser extent raw HCl).

The chemical reactions involved in their production, destruction and fate in the atmosphere is described excellently in the reading.

We focus today and next time on global geochemical topics that are not discussed in much detail in the text:

- patterns of input to the atmosphere
- regional patterns of acid deposition in the world.

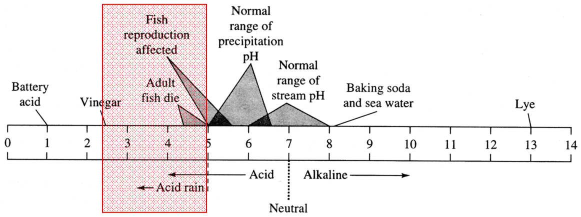


Figure 4-4 pH scale. The normal range of precipitation pH is from about 5.0 to 6.5. The pH of pure water in equilibrium with atmospheric carbon dioxide is 5.6. Normal rain is slightly acidic because of carbon dioxide (which forms the weak acid carbonic acid) and natural emissions of sulfur and nitrogen oxides and certain organic acids. Human activities produce more of these compounds and the result is "acid rain." The formation of strong acids such as sulfuric and nitric acids causes the pH of precipitation to be less than 5.0, producing acid rain. Occasional pH readings of well below 2.4, the acidity of vinegar, have been reported for rain and fog in large cities and highly industrialized areas.

The ingredients in a typical "acid" rain water

Recall that the atmosphere and its waters are naturally acidic due to the presence of CO_2/carbonic acid. CO_2(aq) can also weakly buffer stronger acids by equilibration of carbonate and bicarbonate forms. If enough strong acid is added to bring the solution below pH~ 4.3, these anionic forms are all converted to CO_2 (aq).

CO_2 (aq) concentration is fixed by the Henry's law distribution coefficient between aqueous solution and the atmospheric CO_2 concentration.

The "big 3" atmospheric acids

Hydrochloric acid nitric acid sulfuric acid

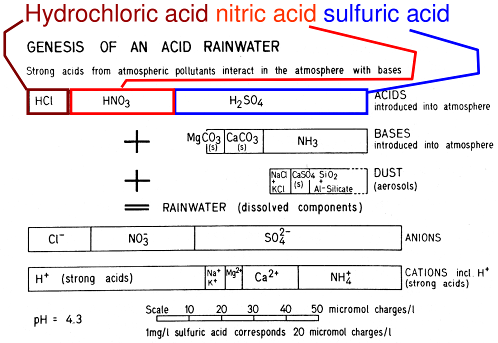


Figure 3.1 Strong acids in rainwater. The acid–base reaction involved in the genesis of a typical acid rainwater. Acids formed from atmospheric pollutants react in the atmosphere with bases and dust particles. The resulting rainwater contains an excess of strong acids. H_2SO_4 originates mostly from S in fossil fuels; after combustion the SO_2 formed is oxidized to SO_3 which gives, with H_2O, H_2SO_4; HNO_3 originates from NO and NO_2. These molecules are formed in the combustion of fossil fuels and to a large extent in the combustion of the automobile engine. For each molecule of NO one of HNO_3 is formed, for example, $NO + O_3 \rightarrow NO_2 + O_2$; $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$. HCl may largely originate from the combustion of Cl-bearing polymers, for example, polyvinyl chloride, in refuse incinerations. Most bases in the atmosphere are often of natural origin. Atmospheric dust may contain carbonates (calcite and dolomite). NH_3 is released from many soils (together with urea). (From J. Zobrist and W. Stumm, *Forschung und Technik*, *Neue Zürcher Zeitung*, June 1979.)

The major "layers" of Earth's atmosphere can be recognized in vertical temperature variations.

Local maxima in temperature correspond to portions of the atmosphere where significant amounts of solar energy are absorbed.

Absorption of energy drives important photochemical reactions, such as oxidation of S and N compounds.

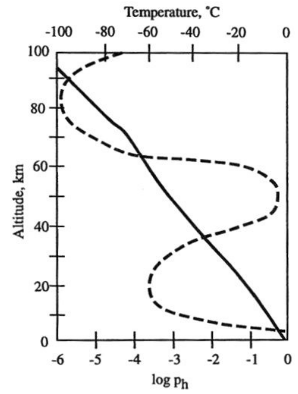


Figure 9.1. Variation of pressure (solid line) and temperature (dashed line) with altitude.

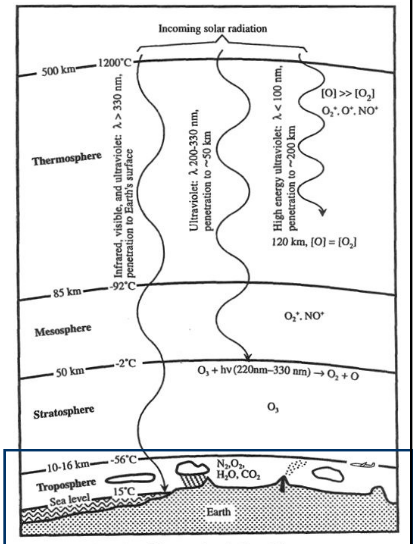


Figure 9.2. Major regions of the atmosphere (not to scale).

We are interested in the troposphere right now

Sources of acidic materials to the atmosphere:

Sulfur

- Fossil Fuel combustion (particularly high sulfur coal) = the major anthropogenic source of SO_2 to the atmosphere.
- Biogenic production of DMS ($S(CH_3)_2$) followed by oxidation by OH• is the main source of biogenic SO_2 in the atmosphere.
- Volcanic Sources involve SO_2, SO_3 and H_2S emissions (the proportions depend on the partial pressure of O_2 and H_2O in a particular magmatic system).

What happens to SO_2 in the atmosphere?

- SO_2 is oxidized to form SO_3 in the atmosphere, which dissolves to make sulfuric acid (an important component of acid rain).
- This occurs mainly in aqueous cloud aerosols where oxidation can be catalyzed by kinetically fast oxidants like H_2O_2.
- Sulfate aerosols contribute to albedo, and are important "nuclei" for cloud formation - a very active area of research in climate science.

What happens to SO_2 in the atmosphere?

Chemical Reactions Summarized

Hydroxyl radical

$SO_2 + 2HO\bullet \rightarrow\rightarrow H_2SO_4$

$SO_2 + H_2O_2 \rightarrow\rightarrow H_2SO_4$

$SO_2 + O_3 \rightarrow\rightarrow SO_3$

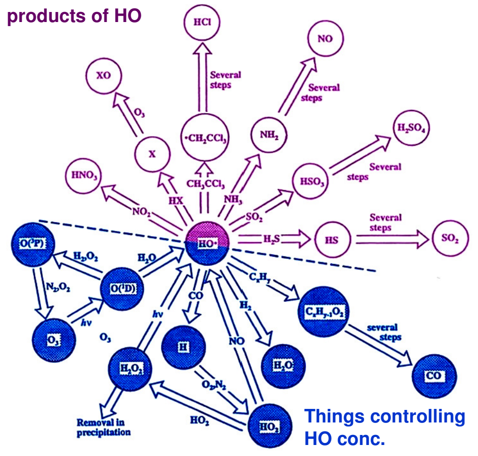
ozone

H_2S -or- $(CH_3)_2S{=}O$ + ($HO\bullet$, H_2O_2 or O_3) 🕓🕓 $SO_3 + SO_2$

dimethyl sulfoxide

$SO_3 + H_2O \rightarrow H_2SO_4$ (sulfuric acid)

$H_2SO_4 \rightarrow H^+ + H\,SO_4^-$

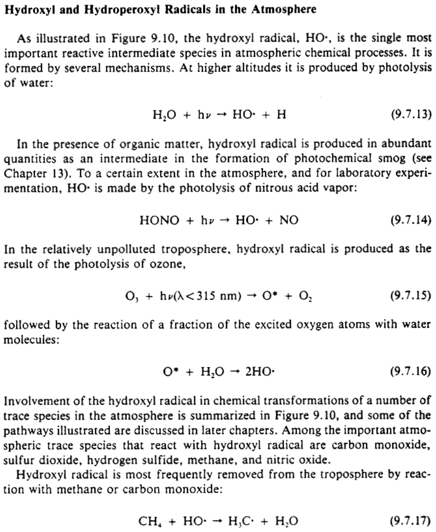


Reactants and products of HO

Things controlling HO conc.

Figure 9.10. Control of trace gas concentrations by HO• radical in the troposphere. Processes below the dashed line are those largely involved in controlling the concentrations of HO• in the troposphere; those above the line control the concentrations of the associated reactants and products. Reservoirs of atmospheric species are shown in circles, reactions denoting conversion of one species to another are shown by arrows, and the reactants or photons needed to bring about a particular conversion are shown along the arrows. Hydrogen halides are denoted by HX and hydrocarbons by H_XY_Y. (Source: D. D. Davis and W. L. Chameides, "Chemistry in the Troposphere," *Chemical and Engineering News*, October 4, 1982, pp. 39-52. Reprinted by permission of the American Chemical Society.)

HO· and HOO· Reactions



Hydroxyl and Hydroperoxyl Radicals in the Atmosphere

As illustrated in Figure 9.10, the hydroxyl radical, HO·, is the single most important reactive intermediate species in atmospheric chemical processes. It is formed by several mechanisms. At higher altitudes it is produced by photolysis of water:

$$H_2O + h\nu \rightarrow HO\cdot + H \quad (9.7.13)$$

In the presence of organic matter, hydroxyl radical is produced in abundant quantities as an intermediate in the formation of photochemical smog (see Chapter 13). To a certain extent in the atmosphere, and for laboratory experimentation, HO· is made by the photolysis of nitrous acid vapor:

$$HONO + h\nu \rightarrow HO\cdot + NO \quad (9.7.14)$$

In the relatively unpolluted troposphere, hydroxyl radical is produced as the result of the photolysis of ozone,

$$O_3 + h\nu(\lambda < 315\ nm) \rightarrow O^* + O_2 \quad (9.7.15)$$

followed by the reaction of a fraction of the excited oxygen atoms with water molecules:

$$O^* + H_2O \rightarrow 2HO\cdot \quad (9.7.16)$$

Involvement of the hydroxyl radical in chemical transformations of a number of trace species in the atmosphere is summarized in Figure 9.10, and some of the pathways illustrated are discussed in later chapters. Among the important atmospheric trace species that react with hydroxyl radical are carbon monoxide, sulfur dioxide, hydrogen sulfide, methane, and nitric oxide.

Hydroxyl radical is most frequently removed from the troposphere by reaction with methane or carbon monoxide:

$$CH_4 + HO\cdot \rightarrow H_3C\cdot + H_2O \quad (9.7.17)$$

Manahan, "Environmental Chemistry"

MSA = CH_3SO_2OH (methanesulfonic acid)
It is relatively stable and mostly “rains out”

The atmospheric sulfur cycle.

Not shown:

Inorganic natural sulfur sources to the atmosphere, which include particulates from “cyclic marine salt” and $CaSO_4$.

Volcanic sources.

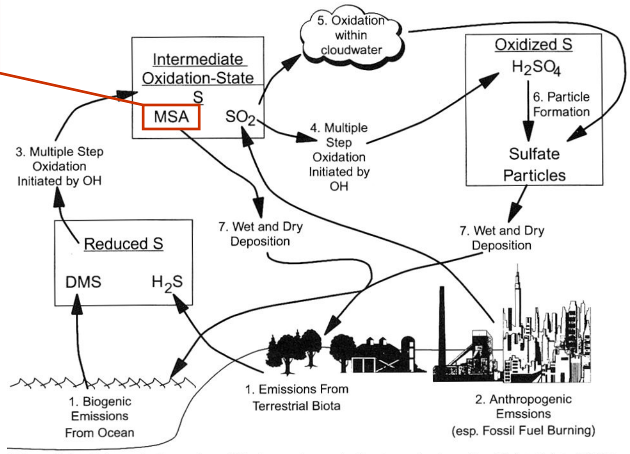


Figure 7.4. Schematic illustration of the key pathways in the atmospheric cycle of S involving: (1) the natural emissions of reduced S compounds such as H_2S from terrestrial biota and dimethylsulfide (CH_3SCH_3) from oceanic biota; (2) anthropogenic emissions of S compounds, principally SO_2; (3) the oxidation of reduced S compounds by OH and other photochemical oxidants leading to the production of intermediate oxidation state S compounds such as SO_2 and methanesulfonic acid (MSA); (4) the oxidation of these intermediate oxidation state compounds within the gas phase by OH-producing H_2SO_4 vapor; (5) the conversion of intermediate oxidation state compounds within liquid cloud droplets, which upon evaporation yield sulfate-containing particles; (6) the conversion of H_2SO_4 to sulfate-containing particles; and (7) the ultimate removal of S from the atmosphere by wet and dry deposition.

Chameides, "Biogeochemical Cycles"

The atmospheric sulfur cycle Quantified

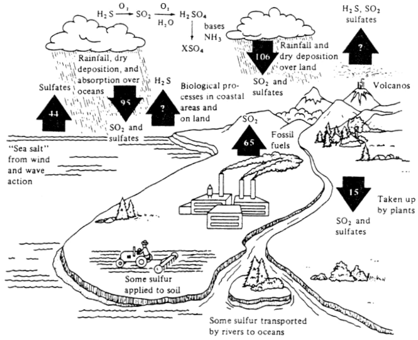


Figure 11.1. The atmospheric sulfur cycle. Quantities are expressed in millions of metric tons per year.

Manahan

Notice the net flux in the atmosphere is from land to sea, which the opposite of the hydrologic cycle

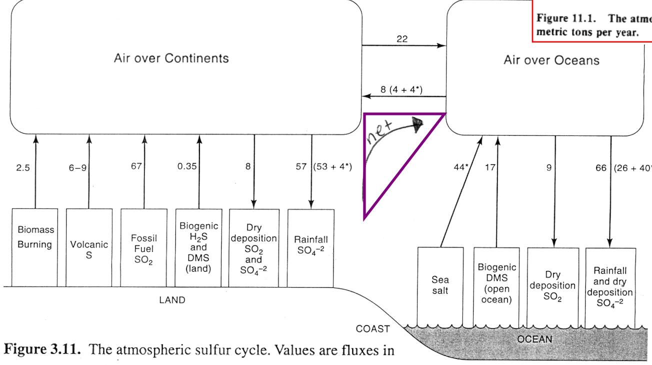


Figure 3.11. The atmospheric sulfur cycle. Values are fluxes in Tg S/yr. Values denoted by an asterisk refer to sea salt.

Tiny reminder of the hydrologic cycle

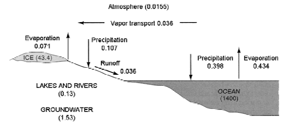


Figure 1.1 The Hydrologic cycle. Numbers in parenthesis represent inventories (in 10^6 km^3 = 10^{18} kg) for each reservoir. Fluxes are in 10^6 km^3/yr (10^{18} kg/yr). (Data from Table 1.1 and NRC 1986.)

Source: Berner and Berner, "Global Environment" (1996) Prentice Hall

Important Atmospheric S Sources by Latitude

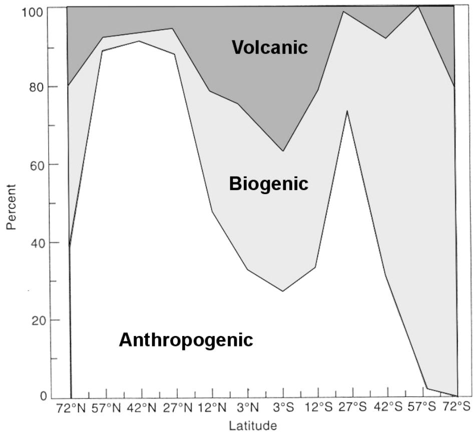


Figure 3.12. Sulfur emissions by latitude and type. The percentage of sulfur emissions from volcanic, biogenic and anthropogenic (fossil fuel combustion + biomass burning) sources in each latitude zone. Latitude zones are 15° wide starting with 80°N–65°N, represented on the graph by its approximate midpoint 72°N, and 65°N–50°N, represented by its midpoint 57°N. The exception is the two zones around the Equator, which are 5°N–0°N and 0°S–5°S. (Data from a model by Bates et al. 1992, Table 6, p. 329.)

Notice that the densely populated northern hemisphere temperate zone produces most of the anthropogenic sulfur flux.

Biogenic Sulfur is another major natural source.

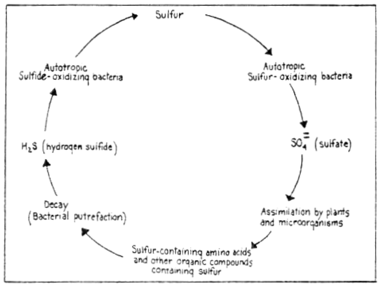
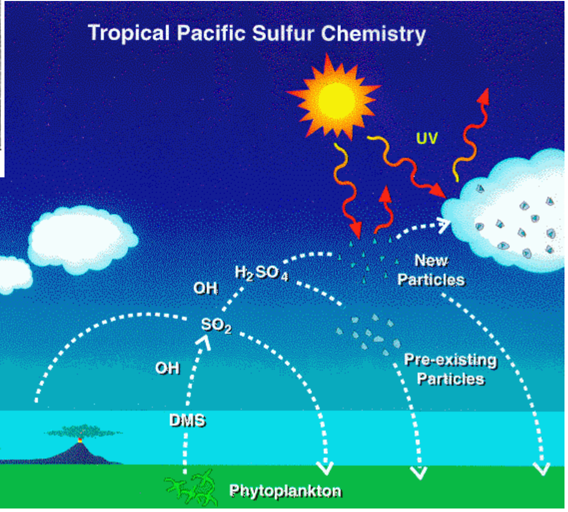


Figure 3–4. The sulfur cycle in the biosphere.

- Gaseous biogenic sulfur is produced from decaying organic matter and humus in soils.
- Biogenic sulfur is also released during forest and grassland fires.



- marine phytoplankton produce DMS as a photosynthetic byproduct.
- DMS is oxidized to SO_2 in the atmosphere.
- The global impact of DMS transport in the atmosphere and it’s effect on the atmospheric energy balance is not completely understood.

The ***volcanic S source***

This is typically introduced *below the tropopause* contributing locally to acid rain waters, acid fog, and sulfate aerosols (a major component of locally well-known VOG).

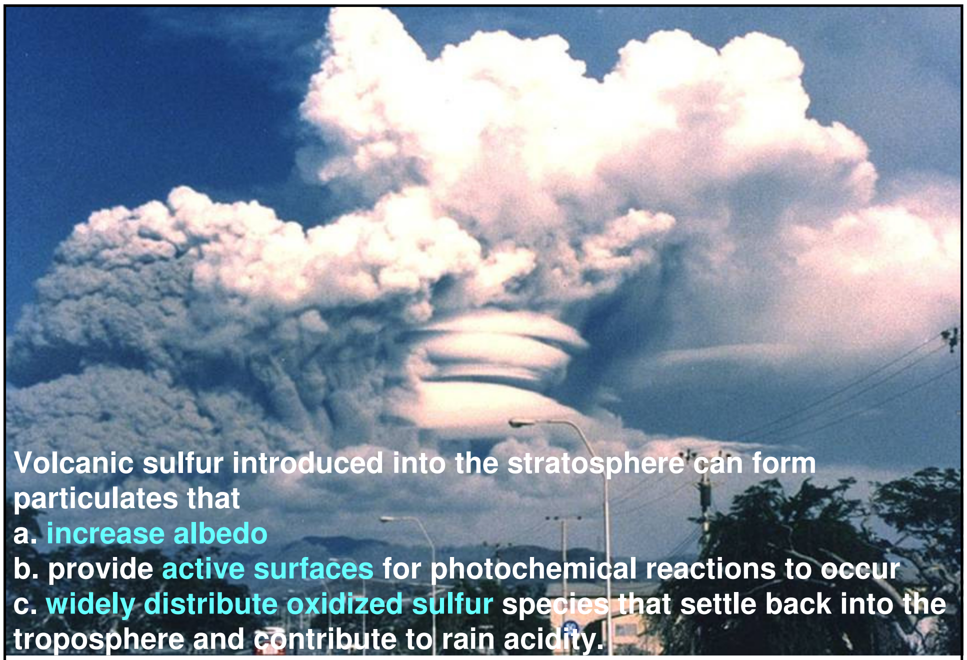
Stratospheric injection is considered on the next slide

A dramatic effect of local S input from Kilauea super-imposed on a rain shadow effect is the Kau desert, a roughly pie-wedge-shaped desert region on otherwise lush Kilauea.


photo by Bruce Houghton

SO_2 plume from Halemaumua, April 2008 (above) –Kau desert (below)


© Dan L. Perlman/EcoLibrary.org



Volcanic sulfur introduced into the stratosphere can form particulates that

a. increase albedo

b. provide active surfaces for photochemical reactions to occur

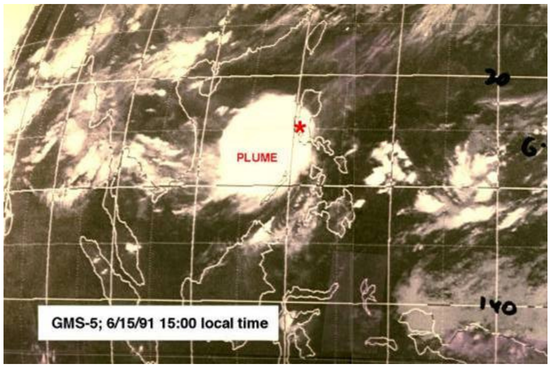
c. widely distribute oxidized sulfur species that settle back into the troposphere and contribute to rain acidity.

Particularly large volcanic events in the past have:

1. left sulfate "spikes" in continental glacial ice cores.

2. contributed to global cooling.

3. accelerated for a brief period of time the rate of continental weathering.



Satellite image of the 1991 Pinatubo eruption plume

Anthropogenic Sources of sulfur.

Anthropogenic sources of S include the smelting and metal refining industry by oxidation of PbS_2, CuS_2, and ZnS_2, among other ores.

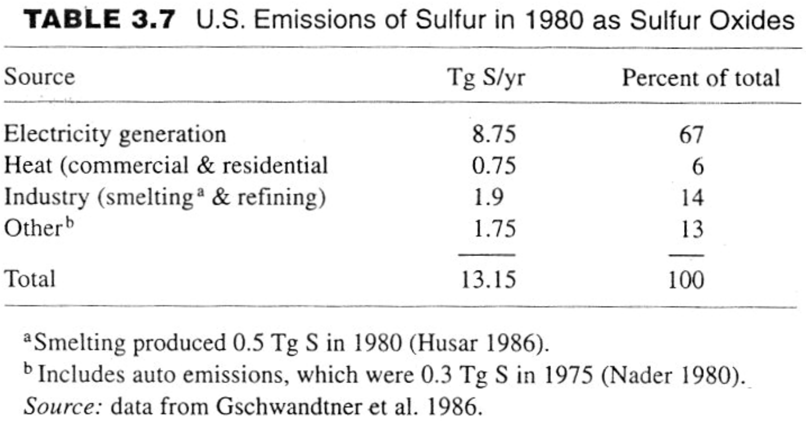


TABLE 3.7 U.S. Emissions of Sulfur in 1980 as Sulfur Oxides

Source	Tg S/yr	Percent of total
Electricity generation	8.75	67
Heat (commercial & residential	0.75	6
Industry (smelting[a] & refining)	1.9	14
Other[b]	1.75	13
Total	13.15	100

[a] Smelting produced 0.5 Tg S in 1980 (Husar 1986).

[b] Includes auto emissions, which were 0.3 Tg S in 1975 (Nader 1980).

Source: data from Gschwandtner et al. 1986.

Anthropogenic Sources **of sulfur.**

Fossil fuel burning, especially coal (derived from terrestrial organic matter) is a major atmospheric S source.

Coal can contain significant pyrite (FeS_2) from originally biogenic S compounds in the organic matter.

The S and C are oxidized as coal is burned:

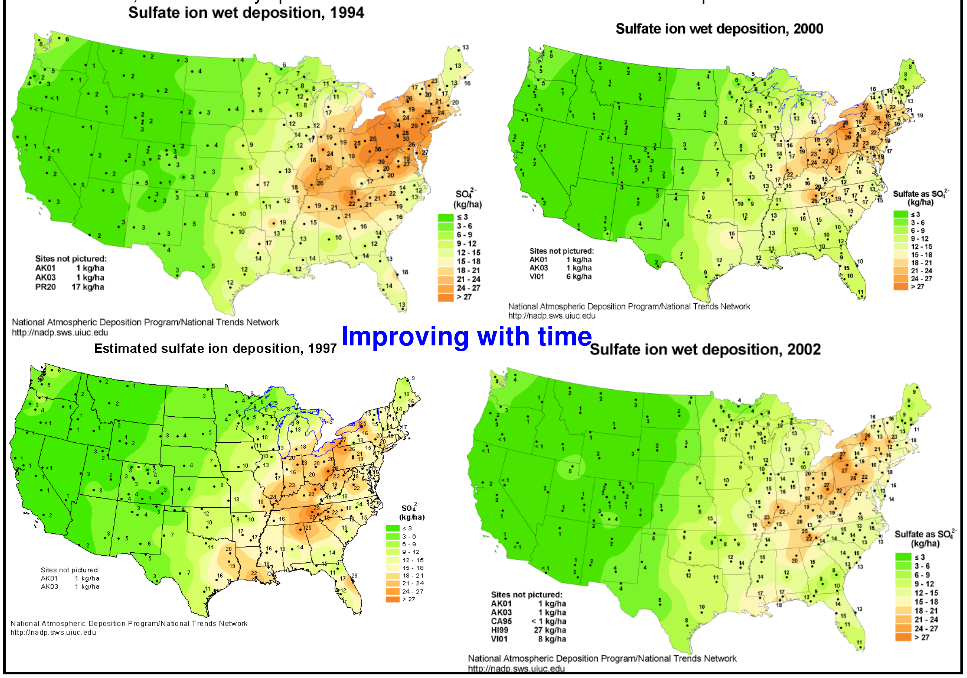
$$C + O_2 + FeS_2 \rightarrow CO_2 + SO_2 + Fe_2O_3$$

This pollutive source can be minimized by using the cleanest coal, or with basic oxide scrubbers on the output gasses of coal-fired industries.

The coal-burning source of atmospheric sulfur was *originally the major source of acid precipitation over the northeastern United States and Northern Europe* throughout most of this century.

Globally, SO_2 from this source is still on the rise, but SO_2 emissions in the wealthier regions of the globe (e.g., the USA) have diminished at the expense of increased NO_2 emissions.

Contours maps of sulfur in recent precipitation over the US. These values are much improved over peak levels in the late 1950's, but the bullseye pattern of enrichment in the northeastern US is still problematic.



Sulfate ion wet deposition, 1994

Sulfate ion wet deposition, 2000

Estimated sulfate ion deposition, 1997

Improving with time

Sulfate ion wet deposition, 2002

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sources of acidic materials to the atmosphere:

Nitrogen

The atmospheric N budget is somewhat more complex because N cycles through the atmosphere/ hydrosphere/biosphere system in large quantities and in many different oxidation states and chemical forms.

Recall that ... Oxidized and reduced N (NO_x, NH_3 and organic bound N) occurs in or can be converted to a number of gaseous forms that are easily exchanged to the atmosphere from soils and the biosphere.

NH_3 vapor dissolves in rain to produce NH_4^+ and OH^- *(base)*

NO_x vapor dissolves in rain to produce NO_3^- and H^+ *(acid)*

(where "NO_x" is any nitrogen oxide gas)

Atmospheric N sources

As discussed previously:

- Natural sources of non-allotropic (N_2) in the atmosphere are essentially all biogenic
- Biogenic NH_3 is the main atmospheric gaseous base.
- There are very few natural oxide sources, primarily oxidation of N_2 during lightening storms and by energetic light in the upper atmosphere.

$$N_2 + O_2 + \text{heat} \rightleftharpoons NO_x$$

Importantly

- Anthropogenic NO_x sources far outweigh natural ones.
- Internal combustion and other form of carbon burning is a main source.
- Much NO_x is produced in association with O_3 and VOC (volatile organic carbon) levels in the lower atmosphere by internal combustion engines.

What happens to NO_x in the atmosphere?

Chemical Reactions Summarized

<u>N</u>: Nitrogen is a second fairly major contributor to atmospheric acidity in excess of that from CO_2. The following reactions summarize its behavior there.

$N_2 + O_2 + \text{heat} \rightarrow\rightarrow NO + N_2O + NO_2 + N_2O_5 = NO_x$

$NO + (HO\bullet, H_2O_2 \text{ or } O_3) \rightarrow\rightarrow NO_2$

$NO + VOC \rightarrow NO_2 + VOC$ (volatile organic carbon)

NO_2 -or- $N_2O_5 \rightarrow HNO_3$ (nitric acid)

$HNO_3 \rightarrow H^+ + NO_3^-$

$NH_3 + H^+ \rightarrow NH_4^+$ (acid neutralization by ammonia)

Changes in NO_3^- distributions in North American Rain between 1955 and 1980.

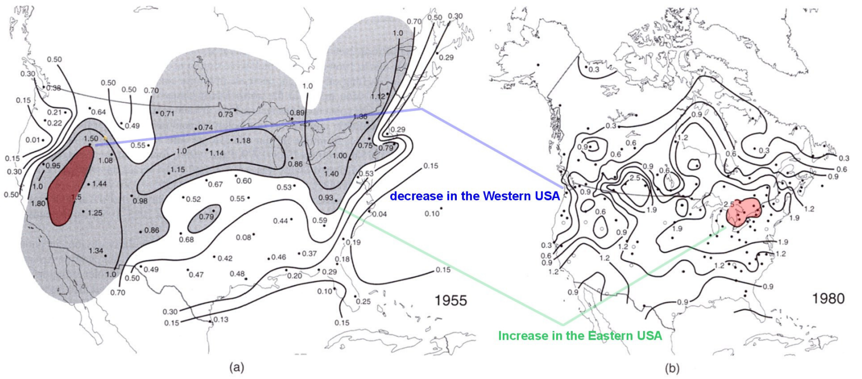
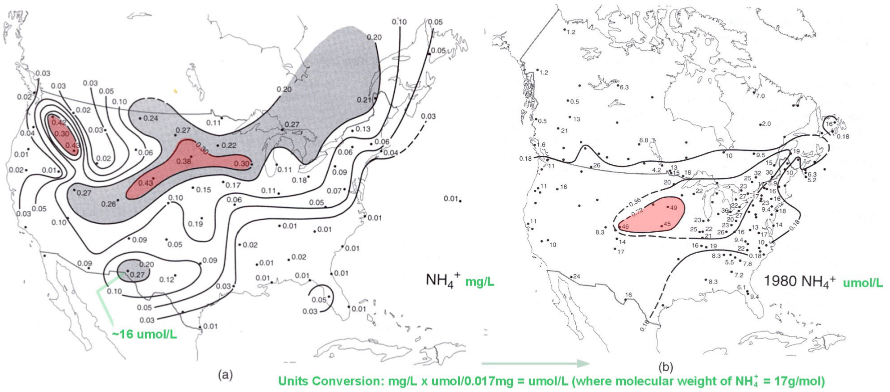


Figure 3.14. Dissolved nitrate (mg/l NO_3^-) in rain over the continental United States and its change with time. (a) Average concentrations, July–September 1955. (After C. E. Junge, "The Distribution of Ammonium and Nitrate in Rain Water over the United States," *Transactions of the American Geophysical Union* 39: 244, © 1958 by the American Geophysical Union.) (b) Average concentrations in 1980 for North America. Open circles indicate stations for which less than 20 weeks' data were available. (Data from National Atmospheric Deposition Program.) [After J. A. Logan, "Nitrogen Oxides in the Troposphere: Global and Regional Budgets," *Journal of Geophysical Research* 88 (C15): 10795, © 1983 by the American Geophysical Union.]

Berner and Berner, "Global Environment"

<u>Nitrate increases in the east</u> and **<u>decreases in the west</u>** due to increased and decreased pollutive input, respectively.

Changes in NH_4^+ distributions in North American Rain between 1955 and 1980.



Units Conversion: mg/L x umol/0.017mg = umol/L (where molecular weight of NH_4^+ = 17g/mol)

Figure 3.16. (a) Ammonium (NH_4^+) concentration in rain over the continental United States (values in mg NH_4^+/l) for July–September 1955. (After C. E. Junge, "The Distribution of Ammonium and Nitrate in Rain Water over the United States," *Transactions of the American Geophysical Union* 39: 242, © 1958 by the American Geophysical Union.) (b) Annual mean precipitation-weighted ammonium concentration (NH_4^+) in North American precipitation in 1980; individual points are in µmol/l; heavy contours are in mg/l. (After Barrie and Hales 1984.)

Berner and Berner, "Global Environment"

Ammonium increases everywhere due primarily to a tripling of the use of ammonium-based fertilizers within the continental US over this time interval.

An aside… Nitrogen-bearing gasses play important roles in numerous troubling environmental phenomena resulting from human activities

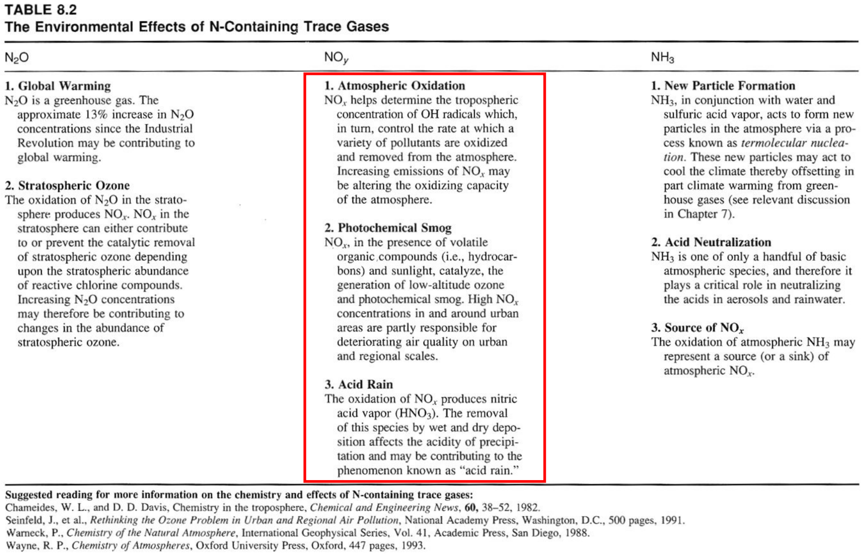


TABLE 8.2
The Environmental Effects of N-Containing Trace Gases

N_2O	NO_y	NH_3
1. Global Warming N_2O is a greenhouse gas. The approximate 13% increase in N_2O concentrations since the Industrial Revolution may be contributing to global warming. **2. Stratospheric Ozone** The oxidation of N_2O in the stratosphere produces NO_x. NO_x in the stratosphere can either contribute to or prevent the catalytic removal of stratospheric ozone depending upon the stratospheric abundance of reactive chlorine compounds. Increasing N_2O concentrations may therefore be contributing to changes in the abundance of stratospheric ozone.	**1. Atmospheric Oxidation** NO_x helps determine the tropospheric concentration of OH radicals which, in turn, control the rate at which a variety of pollutants are oxidized and removed from the atmosphere. Increasing emissions of NO_x may be altering the oxidizing capacity of the atmosphere. **2. Photochemical Smog** NO_x, in the presence of volatile organic compounds (i.e., hydrocarbons) and sunlight, catalyze, the generation of low-altitude ozone and photochemical smog. High NO_x concentrations in and around urban areas are partly responsible for deteriorating air quality on urban and regional scales. **3. Acid Rain** The oxidation of NO_x produces nitric acid vapor (HNO_3). The removal of this species by wet and dry deposition affects the acidity of precipitation and may be contributing to the phenomenon known as "acid rain."	**1. New Particle Formation** NH_3, in conjunction with water and sulfuric acid vapor, acts to form new particles in the atmosphere via a process known as *termolecular nucleation*. These new particles may act to cool the climate thereby offsetting in part climate warming from greenhouse gases (see relevant discussion in Chapter 7). **2. Acid Neutralization** NH_3 is one of only a handful of basic atmospheric species, and therefore it plays a critical role in neutralizing the acids in aerosols and rainwater. **3. Source of NO_x** The oxidation of atmospheric NH_3 may represent a source (or a sink) of atmospheric NO_x.

Suggested reading for more information on the chemistry and effects of N-containing trace gases:

Chameides, W. L., and D. D. Davis, Chemistry in the troposphere, *Chemical and Engineering News*, **60,** 38–52, 1982.
Seinfeld, J., et al., *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D.C., 500 pages, 1991.
Warneck, P., *Chemistry of the Natural Atmosphere*, International Geophysical Series, Vol. 41, Academic Press, San Diego, 1988.
Wayne, R. P., *Chemistry of Atmospheres*, Oxford University Press, Oxford, 447 pages, 1993.

The relationship between O_3, VOC and NO_x is complicated and simply diminishing one reactant or another doesn't always reduce tropospheric O_3.

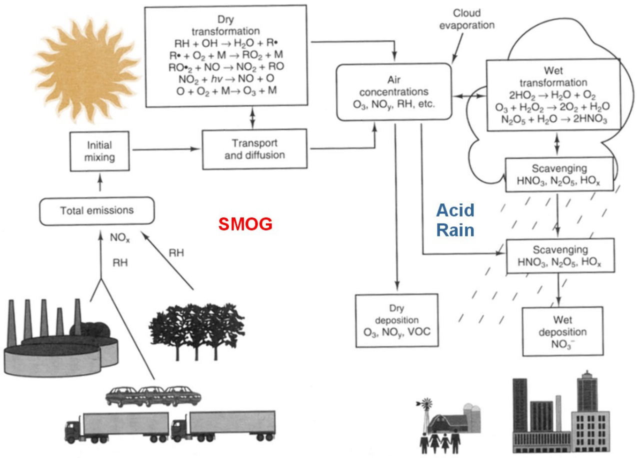
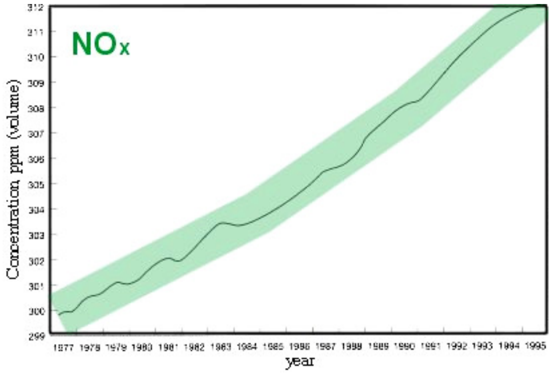


FIGURE 9–4 Photochemical air pollution, from emission to deposition. See Appendix 9–1 for discussion of reactions. NO_y includes volatile HNO_3, as well as NO and NO_2. (From National Research Council Report, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, 1991, National Academy Press.)

Turekian, "Global Environmental Change"

In order for ozone-containing smog to form at high levels, relatively stagnant air containing VOC, NO_x, and low humidity must be subjected to sunlight. If humidity is too high, NO_x is instead removed to produce HNO_3 rich rain.

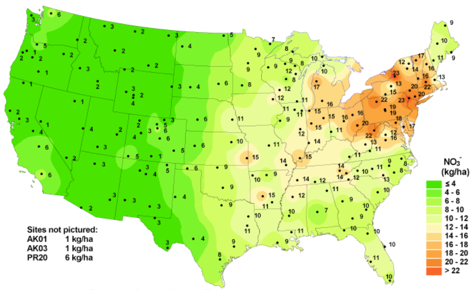
Atmospheric NOx input is still on the rise, both in the US and globally



Atmospheric nitrous oxide levels from 1975 to 1994 (after Heilman, 1989; Boden et al., 1991; Prinn et al., 1990; Houghton et al, 1996).

Unlike SO_2, anthropogenic nitrogen oxide inputs to the atmosphere are more evenly distributed and not quite so "point-source" in style. Never-the-less, the eastern US is still the main source in the country of both of these contaminants to the atmosphere today (80% of the SO_3 and 65% of the NO_x are produced east of the Mississippi).

Nitrate ion wet deposition, 1994



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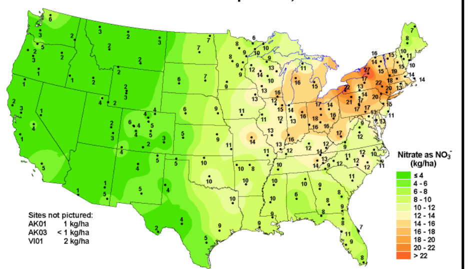
Nitrate ion wet deposition, 2000



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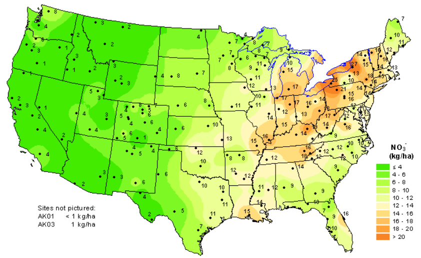
http://nadp.sws.uiuc.edu

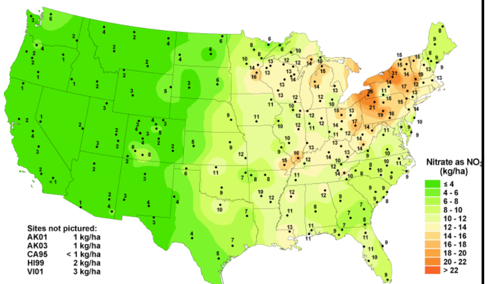
Improving with time (mostly)

Estimated nitrate ion deposition, 1997



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Nitrate ion wet deposition, 2002



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sources of acidic materials to the atmosphere:

Chlorine

Cl is not a major contributor to acidity in the atmosphere.

It is found usually as Hydrochloric acid or hypochlorous acid. The major natural source of HCl is volcanic gasses.

Cl_2 released by industrial practices will be oxidized and reduced to HOCl and Cl^- by H_2O droplets.

Additionally, waste incineration of chlorinated hydrocarbons and polymers such as PVC produce HCl.

Chemical Reactions Summarized

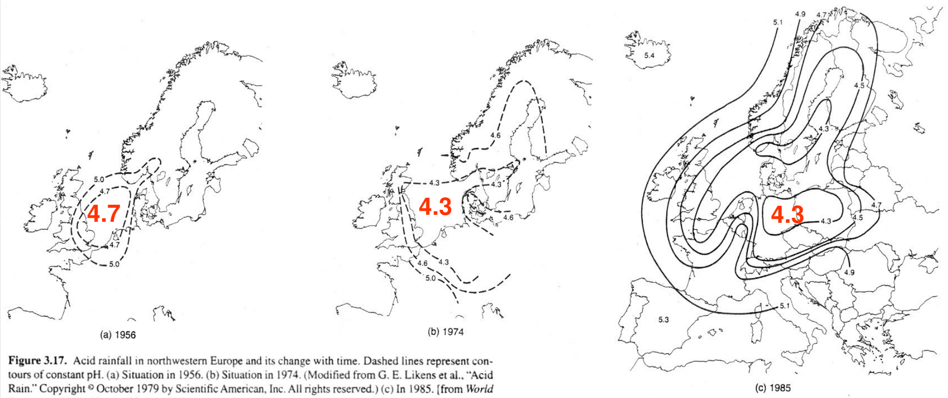
HCl → H+ + Cl-

Cl_2 + H_2O → H+ + Cl- + HOCl

Global Patterns of Acid Oxide Production and Rain

Anthropogenic NO_x and SO_2 (and HCl) inputs to the atmosphere have resulted in acidic rain over much of the industrialized world.

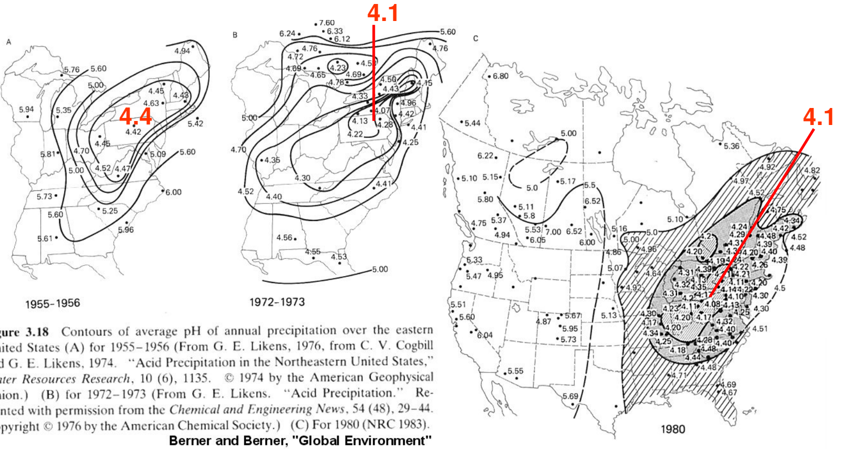
<u>Long term trends in Rain pH over Europe:</u>



(a) 1956 (b) 1974 (c) 1985

Figure 3.17. Acid rainfall in northwestern Europe and its change with time. Dashed lines represent contours of constant pH. (a) Situation in 1956. (b) Situation in 1974. (Modified from G. E. Likens et al., "Acid Rain." Copyright © October 1979 by Scientific American, Inc. All rights reserved.) (c) In 1985. [from *World Resources 1988–89*, Fig. 23.2, p. 337. *Source:* Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP); Summary Report from the Chemical Coordinating Centre for the Third Phase of EMEP (Norwegian Institute for Air Research, Lillestrom, *Norway*, 1987).]

<u>Long term trends in Rain pH over the US:</u>



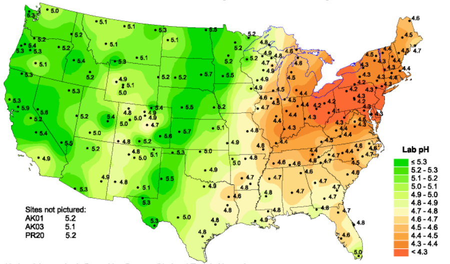
1955–1956 1972–1973 1980

Figure 3.18 Contours of average pH of annual precipitation over the eastern United States (A) for 1955–1956 (From G. E. Likens, 1976, from C. V. Cogbill and G. E. Likens, 1974. "Acid Precipitation in the Northeastern United States," *Water Resources Research*, 10 (6), 1135. © 1974 by the American Geophysical Union.) (B) for 1972–1973 (From G. E. Likens. "Acid Precipitation." Reprinted with permission from the *Chemical and Engineering News*, 54 (48), 29–44. Copyright © 1976 by the American Chemical Society.) (C) For 1980 (NRC 1983).

Berner and Berner, "Global Environment"

Coal-burning was originally the major source of acid precipitation over the northeastern United States and Northern Europe throughout most of the last century.

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1994



Sites not pictured:
AK01 5.2
AK03 5.1
PR20 5.2

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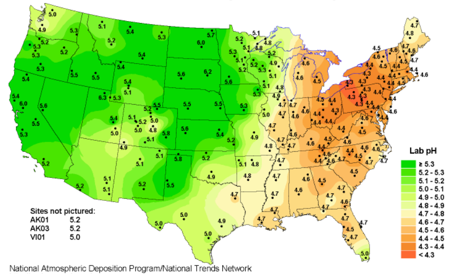
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2000



Sites not pictured:
AK01 5.2
AK03 5.2
VI01 5.0

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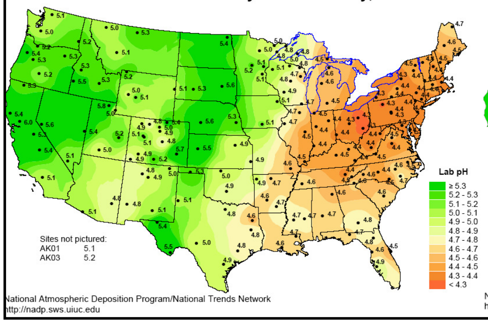
More Recent Trends over the US - **Improving slightly with time**

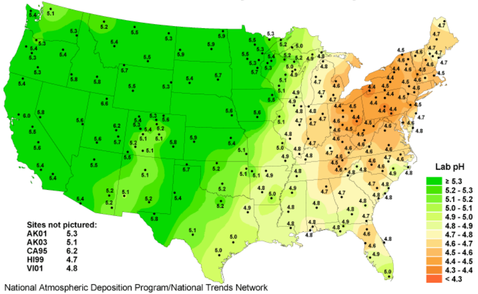
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1997



Sites not pictured:
AK01 5.1
AK03 5.2

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2002



Sites not pictured:
AK01 5.3
AK03 5.1
CA95 6.2
HI99 4.7
VI01 4.8

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

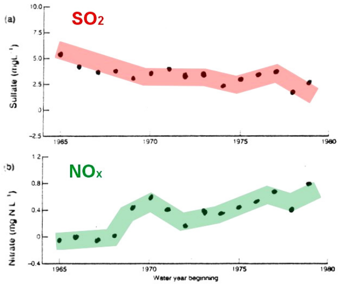
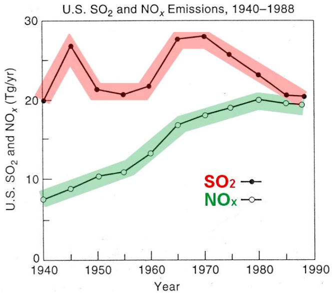


FIGURE 9–2 Changes in precipitation chemistry at the Hinckley, New York, USGS site. (a) Sulfate concentration, and (b) nitrate concentration. Data are from monthly bulk-deposition samples. (Summary from National Research Council Report, *Acid Deposition*, 1986, National Academy Press.)

A comparison of [SO_4^{2-}] and [NO_3^-] concentrations in rain water from a site in New York state demonstrates that sulfate has been dropping in rain since 1965, whereas nitrate is on the rise.

A similar trend is seen in US emissions of sulfur and nitrogen oxides and for SO_2 in the UK in the last half of the century

These (wealthier) regions of the globe have diminished SO_2 output at the expense of increased NO_2 emissions



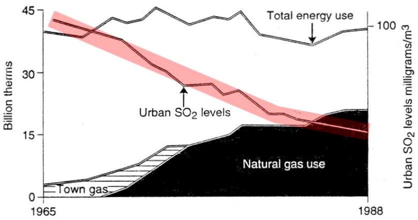


Fig. 4.2 Reduction of urban sulphur dioxide (SO_2) levels compared with increasing use of natural gas. (From Department of the Environment Digest of UK Energy Statistics, HMSO, 1990.)

Figure 3.8. Rise in U.S. emissions of SO_2 and NO_x from 1940 to 1988. Top curve: U.S. SO_2; bottom curve: U.S. NO_x. To compare SO_2 data here with data given elsewhere in the present chapter, divide by 2 to obtain Tg S/yr. (*Sources:* Gschwandtner et al. 1986; *World Resources 1992–93*, p. 351.)

Globally, both SO_2 and NO_x production are still on the rise

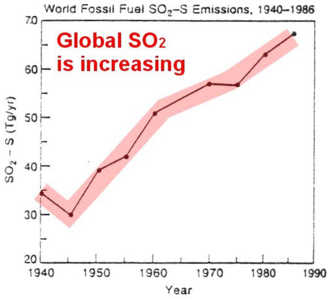


Figure 3.9. World fossil fuel emissions from 1940 to 1986 in Tg SO_2-S/yr. [Data from Möller (1984) for prior to 1970; data for 1970 and thereafter from Hameed and Dignon (1992).]

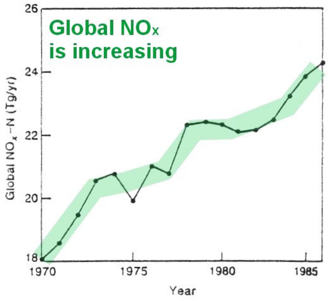


Figure 3.15. Worldwide production of NO_x-N by fossil fuel emissions from 1970 to 1986 in Tg N/yr. (Data from Hameed and Dignon 1992.)

Effects of acid precipitation on the environment.

Chemical-Geological

Acid precipitation has little affect on the oceans because they are large and at basic pH.

In contrast, high acidity affects the stability of natural compounds in the “fresh” hydrosphere.

Soils and sedimentary deposits with fine-grained solids are one of the first geologic entities to interact with acidic rain water.

High CEC soils and sediments are more immune to the ill-effects of acid precipitation and better protect watershed flora and fauna from acid precipitation

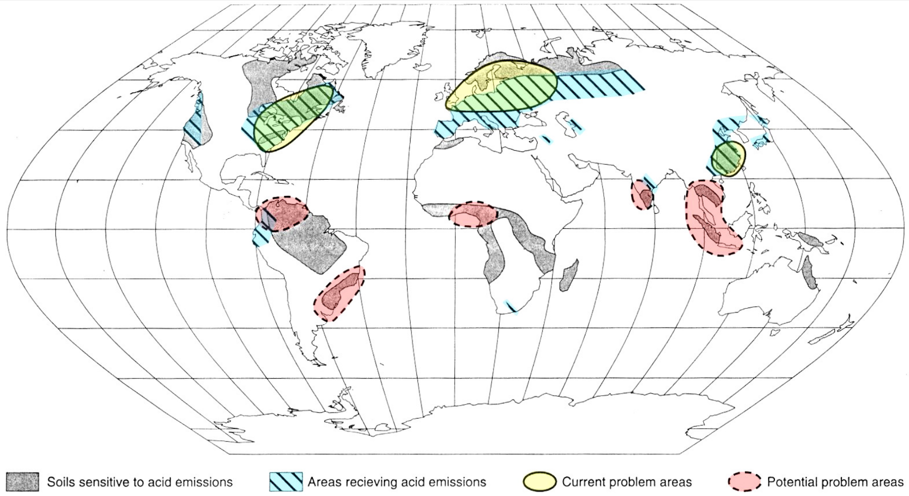


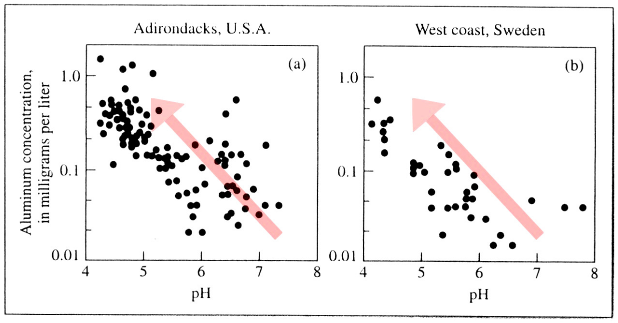
Figure 3.18. World areas with present or future acid deposition problems. (a) Areas, circled by solid lines, that *presently* have a problem with anthropogenic acid (sulfur and nitrogen) emissions due to sensitive soils and (b) *potential* problem areas (circled by dashed lines)—areas with sensitive soils that have or are expected to have rapidly growing acid emissions. (*Source:* Adapted from Rodhe 1989.)

☐ In practice, soils with a CEC > about 15 meq/100 g are insensitive to acid precipitation.
☐ Soils with 15 > CEC > 6 are somewhat sensitive to acid precipitation.
☐ Soils with CEC < 6 are very sensitive to acid precipitation.

The presence or absence of carbonate minerals also contributes to soil sensitivity. *Soils <u>help to buffer ground water</u> produced from acid rain:*

- ☐ by the dissolution of basic (carbonate and hydroxide) minerals
- ☐ by protonation of organic matter
- ☐ by cation exchange of hydrogen ions with clay minerals in the soil.

By doing these things soils "protect" the rest of the hydrosphere from the low pH of acid rain. This buffering of acid rain by soil has negative effects, such as:



☐ release of Al^{+3} into soils, with toxic effects for land plants

[continued on next page]

Figure 3-5
Aluminum concentrations versus pH of the water in different freshwater lakes in (a) the Adirondacks and (b) western Sweden. Notice the logarithmic vertical axis. (Source: M. Havas and J. F. Jaworski. 1986. *Aluminum in the Canadian Environment*. National Research Council of Canada NRCC Report 24759.)

More negative effects of acid rain buffering by soil:

- liberation of ions from basic hydroxide and carbonate precipitates formed during rock weathering, diminishing the capability of a soil to regulate it's pH

- protonation of organic substances in soils and natural waters, limiting their ability of to chelate trace metals.

- protonation of clay minerals, limiting a soil's capacity to hold nutrient ions used by plants.

Negative effects of acid precipitation on the ***anthrosphere****:*

- Acid rain also causes corrosion of metal surfaces and the dissolution of some paints, releasing toxic metals and organic compounds into the environment.

More Negative effects of acid precipitation on the ***anthrosphere****:*

- Acid rain and snow are harmful to manmade structures such as buildings and statues made of various forms of $CaCO_3$ (e.g., marble, limestone, travertine).

These photos demonstrate that acid rain corrosion of marble can be rapid (the photo on the left was taken around 1908; the photo on the right was taken in 1969).

A limestone sculpture fronting the St. Peter and St. Paul church in Cracow, Poland. Acid rain has damaged this sculpture (left). Compare to the copy made to replace the original (right). Copies have also been made to replace the other eleven apostle sculptures at this church.

http://www.atmosphere.mpg.de/enid/3vq.html photos: Sebastian Wypych

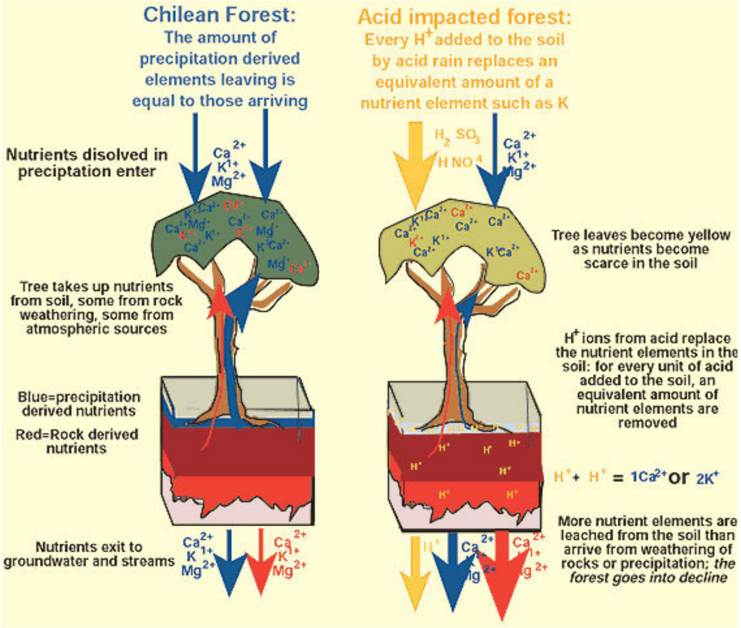
Effects of acid precipitation on the environment.

Biological effects: Yesterday we noted large impacts of acid rain on aquatic ecosystems. There are also impacts to terrigenous habitats. Acid rain (plus dry deposition of SO_2 aerosols) has had detrimental effects on land plants, including large scale reduction of forests in Western Europe and the Eastern US (and to a lesser extent in the western US). Acid rain …

- damages tree leaves
- makes plants more susceptible to disease and insects
- affects nutrient cycling in soils.

Tree dieback in Ohio due to acid rain

Effects of acid precipitation on the environment.



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