Acid Rain
These notes are from 2010

Cap and Trade Working Already
December 15, 2009 10:14 AM - *Roger Greenway, ENN*

The US already has years of experience with Cap and Trade. A sulfur dioxide (SO_2) Cap and Trade program has proven an effective control strategy to lower SO_2 emissions. It provides elements of market incentives and provides flexibility to facilities that emit large quantities of the pollutant in several ways. One of the most important ways is that it permits older facilities which may need to operate for a limited number of years to purchase "emissions credits" to continue operating without installing un-economic emissions controls by purchasing credits. The credits are created by other sources which control their emissions MORE than required under regulations. There is also an overall reduction in the program to benefit the environment so we are not just transferring emission from one plant to another. A reflection of the effectiveness is that the U.S. Environmental Protection Agency announced that power plants across the country decreased emissions of SO_2, a precursor to acid rain, to 7.6 million tons in 2008.

Overview of Acid Rain Phenomenon

Most common term for acidification of the environment, which can occur from a wide variety of processes, including precipitation, fog, dry deposition, aerosol sedimentation

Acids in the environment originate largely from pollutants such as nitrogen and sulfur oxides, which, in turn are generally by-products of combustion activities

Research into environmental acidity started in the late 1800's in Britain and Scandinavia; widespread effects seen as early as the 1950's

The first large-scale (multi-national) environmental issue, requiring cooperation among states and countries (e.g., US and Canada)

Effects include "death" of many mountain lakes and severe damage to forests

Good case study in regulation and international cooperation

The Basics: Acidity and pH

Need a refresher on acid/base chemistry? Try this web based <u>tutorial</u>!

Recall that water dissociates weakly: $H_2O \rightarrow OH^- + H^+$

<u>What is an acid?</u> - A substance that, when dissolved in water, increases the concentration of hydrogen ion (H^+). Similarly a <u>base</u> is a substance that, when dissolved in water, increases the concentration of the hydroxide ion (OH^-).

In an acidic solution, $[H^+] > 1.00 \times 10^{-7}\ M$ ($M \equiv$ moles L^{-1})

In a neutral solution, $[H^+] = 1.00 \times 10^{-7}\ M$

In a basic solution, $[H^+] < 1.00 \times 10^{-7}\ M$

The pH scale

For convenience, the pH (potential hydrogen) scale was developed. This relates the $[H^+]$ to an easier number to manipulate, via:

$$pH = -\log_{10}[H^+]$$

So, if the $[H^+]$ of a solution is 1×10^{-4} *M*, the pH would be

$$pH = -\log_{10}(1 \times 10^{-4}) = 4$$

If the $[H^+]$ of a solution is 1×10^{-3} *M*, the pH would be

$$pH = -\log_{10}(1 \times 10^{-3}) = 3$$

If the [H+] is 3×10^{-4} *M*, the pH would be somewhere in between:

$$pH = -\log_{10}(3 \times 10^{-3}) = 3.52$$

Acids (and Bases) in Water

Called aqueous solutions; ions given subscript (aq)
Let's take a generic acid, HA:

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]}$$

Since the water concentration does not change (it is 55.5 moles L^{-1}. since there is 1 kg of water in 1 L), it can be combined with K:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

The chemical equation is typically shortened to $HA_{(aq)} \leftrightarrow H^+_{(aq)} + A^-_{(aq)}$

so $K_a = [H^+][A^-]/[HA]$

What about [OH]$^-$?

Called the self-ionization of water, to some small degree, water will break down into ions as well. So water has its own equilibrium constant:

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \, M^2$$

So if pH = 7

$$[H^+] = 1 \times 10^{-7} \, M$$

$$[OH] = 1 \times 10^{-14} \, M^2 / (1 \times 10^{-7} \, M) = 1 \times 10^{-7} \, M$$

$$pOH = -\log_{10}[OH^-] = 7$$

This result is nice, because we can always calculate [OH$^-$] if we know [H$^+$].

Sample Problem: The pH of blood is 7.40. What is the hydrogen ion concentration? What is the hydroxide ion concentration?

$pH = -log[H^+]$, so $[H^+] = 10^{-pH}$

$[H^+] = 10^{-7.4} = 3.98 \times 10^{-8}$ *M*

To determine the $[OH^-]$, one can take either of two paths:

(a) $pH + pOH = 14.0$, so $pOH = 14.0 - pH = 6.6$
    Then $[OH^-] = 10^{-pOH} = 10^{-6.6} = 2.51 \times 10^{-7}$ M

(b) $[H^+][OH^-] = 1 \times 10^{-14}$, so $[OH^-] = 1 \times 10^{-14}/[H^+]$
    Then $[OH^-] = 1 \times 10^{-14}/3.98 \times 10^{-8} = 2.51 \times 10^{-7}$ M

We typically deal with two classes of acids.

For strong acids, $K_a \gg 1$ (can even assume infinity!)

So that the demoninator is so small that essentially the acid completely dissociates into ions.

For weak acids, K_a is finite, and there will be some undissolved parent acid (HA) in solution. We can use the equilibrium (or acidity) constant to determine the ions in solution, although the math may be a bit cumbersome (involving a quadratic expression).

Sample of a Weak Acid Problem

A 0.01 *M* solution of hydrofluoric acid (HF) is used in an experiment. If $K_a = 6.8 \times 10^{-4}$, what is the pH of this solution?

$$HF \leftrightarrow H^+_{(aq)} + F^-_{(aq)}$$

initial: 0.01   0   0

change: $-x$ $+x$ $+x$

final: 0.01-x   x   x
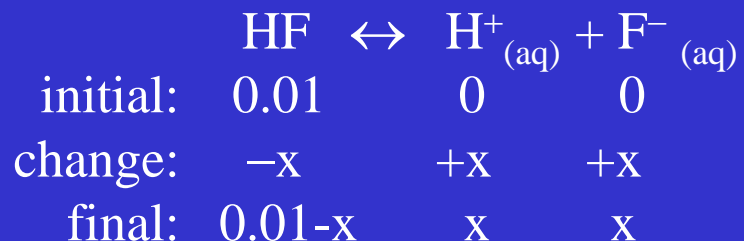
Then,

$$K_a = [H^+][F^-]/[HF]$$

$$6.8 \times 10^{-4} = x^2/(0.01-x)$$

If x is small compared to 0.01, we can disregard it in the denominator.

$$x^2 = 6.8 \times 10^{-6}$$
$$x = 2.61 \times 10^{-3} \, M$$
$$pH = -\log[2.61 \times 10^{-3}] = 2.58$$

Note that we can solve this exactly by using the quadratic equation:

$$6.8 \times 10^{-4} = x^2/(0.01-x)$$

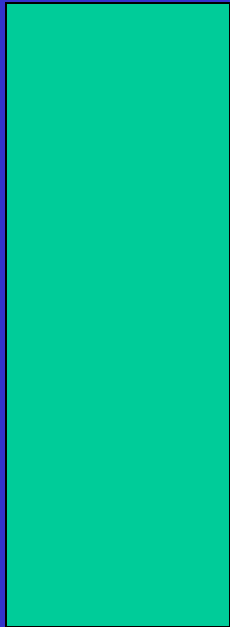$$x^2 + 6.8 \times 10^{-4}\, x - 6.8 \times 10^{-6} = 0$$

Solve for $x = 2.29 \times 10^{-3}$ M

pH = 2.64

the answer on the previous pages off by only a little – about 12%

Symbolically

Before

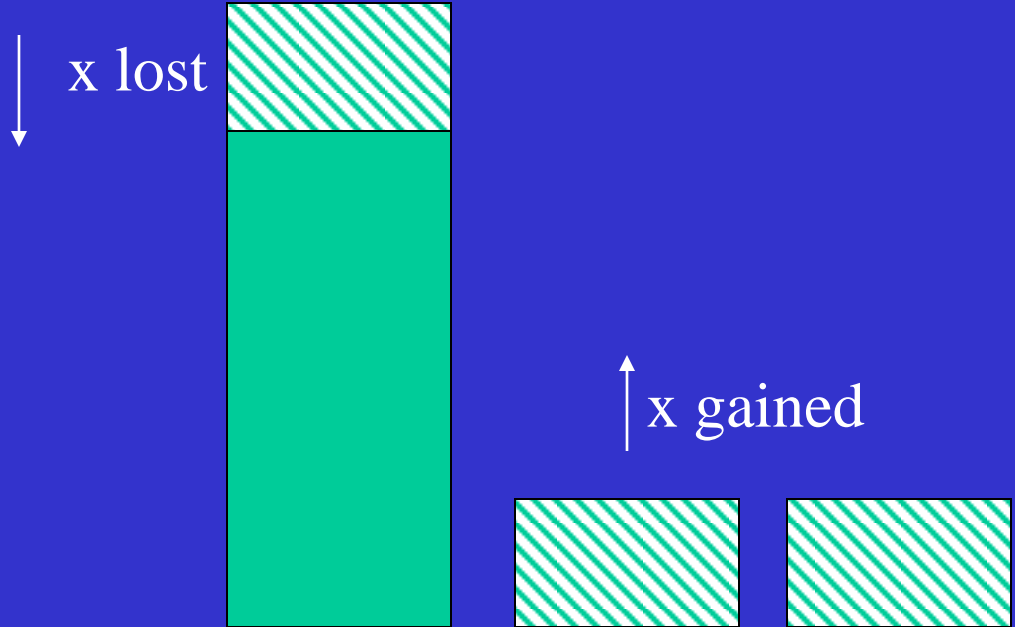After

x lost

x gained

[HA]   [H$^+$]   [A$^-$]   [HA] $_{(aq)}$ [H$^+$]   [A$^-$]

Atmospheric Aqueous Chemistry

Atmospherically relevant aqueous chemistry usually involves interactions between gases and water, in addition to the liquid-phase reactions.
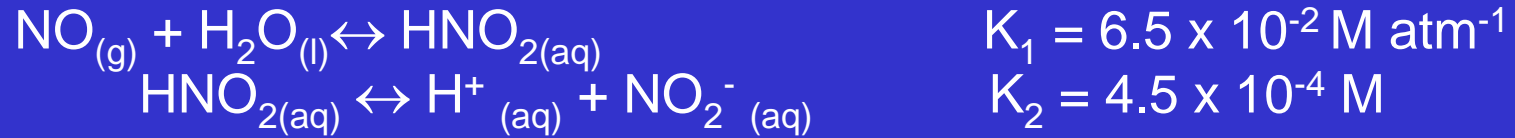
When a gas is involved, we use its partial pressure rather than concentration:

$$G_{(g)} + H_2O_{(l)} \leftrightarrow GH_{(aq)} \qquad\qquad K_h = [GH]/p_G$$

K_h for this type of situation is called the "Henry's Law Constant"

Note that this equilibrium is a bit different than our analysis of heterogeneous reactions from last lecture. Here, we assume that a gas is partitioned between the gas and aqueous phases. In the atmosphere, acids typically stick to water droplets, so we are mainly interested in how many of those molecules come back out of solution once they are dissolved. Most strong acids don't return to the gas phase (i.e., K >>1), but some (like CO_2) do.

Example: Nitrogen oxides can interact with water to produce nitrous acid:

$$NO_{(g)} + H_2O_{(l)} \leftrightarrow HNO_{2(aq)} \qquad\qquad K_1 = 6.5 \times 10^{-2} \text{ M atm}^{-1}$$
$$HNO_{2(aq)} \leftrightarrow H^+_{(aq)} + NO_2^-_{(aq)} \qquad\qquad K_2 = 4.5 \times 10^{-4} \text{ M}$$

Suppose there were a raindrop in contact with these gases; what would its pH be? [NO = 1×10^{-9} atm]

First, set up equilibrium expressions for the two processes:

$$K_1 = [HNO_2]/P_{NO} \qquad\qquad K_2 = [H^+][NO_2^-]/[HNO_2]$$

Both expressions contain $[HNO_2]$, so we can solve one and substitute into the other:

$$[HNO_2] = K_1 P_{NO} \qquad\qquad \text{then } K_2 = [H^+][NO_2^-]/K_1 P_{NO}$$

However, this still leaves us with an equation with two unknowns. From the second chemical reaction, we can see that for every H^+, we must have an NO_2^-. In other words, $[H^+] = [NO_2^-]$. This allows us to simplify the equation for K_2 to:

$$K_2 = [H^+][H^+]/K_1\, P_{NO}$$

Solving for $[H^+]$:

$$[H^+]^2 = K_2\, K_1\, P_{NO}$$

$$[H^+] = (K_2\, K_1\, P_{NO})^{1/2}$$
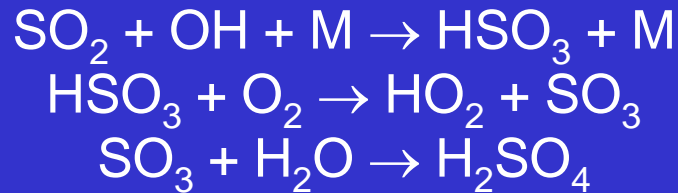
$[H^+] = [(6.5 \times 10^{-2}\, M\, atm^{-1})(4.5 \times 10^{-4} M)(1 \times 10^{-9}\, atm)]^{1/2} = 1.7 \times 10^{-7}\, M$

$pH = -\log[H^+] = -\log[1.7 \times 10^{-7}] = 6.77$

What are the acids in the atmosphere?

Inorganic acids

Sulfuric acid (H_2SO_4): Source – sulfur-containing gases such as SO_2, H_2S, and $(CH_3)_2S$ (dimethyl sulfide)

$$SO_2 + OH + M \rightarrow HSO_3 + M$$
$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Nitric acid (HNO_3): Source – nitrogen oxide emissions from combustion and soils

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

Hydrochloric acid (HCl): Source – Volcanoes, industry

Carbonic acid (H_2CO_3): Source – carbon dioxide, mostly natural, but has increased due to fossil fuel burning

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Sulfurous acid (H_2SO_3): Source – sulfur dioxide (as above)

$$SO_2 + H_2O \leftrightarrow H_2SO_3$$

Organic acids – Origins can be biologic or fossil-fuel emissions

Formic acid (HCOOH): Source – by-product of oxidation of complex hydrocarbons; also made by ants

Acetic acid (CH_3COOH): Also a by-product of oxidation

So "clean" water in the atmosphere is made slightly acidic through contact with CO2, which forms an acid when it dissolves in water.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad K_1 = 3.45 \times 10^{-2} \text{ moles } L^{-1} \text{ atm}^{-1}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

For the atmosphere, we can typically stop at the second step above in order to get a good estimate for the pH of water in contact with CO_2. The first step, dissolution of CO2 in water, can be calculated using the expression:

$$K_1 = [H_2CO_3] / p_{CO2} = 3.45 \times 10^{-2} \text{ moles } L^{-1} \text{ atm}^{-1}$$

Where p_{CO2} is the partial pressure of CO_2, which is basically the mixing ratio, or 0.000400 atm for "400 ppm"

So $[H_2CO_3]$ = $3.45 \times 10^{-2} \times 0.000400$ moles L^{-1}

$$= 1.38 \times 10^{-5} \text{ moles } L^{-1}$$

Based on the equilibrium for the second step:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$K_2 = [HCO_3^-] [H^+]/ [H_2CO_3] = 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

But each time H_2CO_3 dissolves, it makes one HCO_3^- and one H^+, so $[HCO_3^-] = [H^+]$

$$[H^+]^2/ [H_2CO_3] = 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$[H^+]^2 = [H_2CO_3] \times 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$= 1.38 \times 10^{-5} \text{ moles L}^{-1} \times 4.45 \times 10^{-7} \text{ moles L}^{-1}$$

$$= 6.14 \times 10^{-12} \text{ (moles L}^{-1})^2$$

Taking square root, $[H^+] = 2.48 \times 10^{-6} \text{ moles L}^{-1}$

$$pH = 5.61$$

Note

Remember back at the start of the course we stopped the methane oxidation cycle at formaldehyde? This was because it is very often the case that once an organic molecule begins to be oxidized (as oxygen atoms are added to the chain), the molecules become more soluble in water, and in the presence of wet particles they will partition into the aqueous phase. This changes the oxidation process, shifting the role of oxidant from gas-phase OH to strong acid species (like SO_4^- or NO_3^-) that are found in particles)

What's in acid rain? Short answer – it depends on the location!!

North America:
> Mostly sulfate (SO_4^{2-}), followed by nitrate (NO_3^-) and chloride (Cl^-). Some regional dependence – more chloride near coasts, more nitrate in heavily polluted areas (such as LA)
> Cations (to balance charge): Na^+, Ca^{2+}, NH_4^+

Europe:
Similar to the US

China:
> In some regions, acidity neutralized by alkaline dusts from the central desert.
> Otherwise, afflicted with the same problems as industrialized areas.

Remote regions: (northern Canada, central Australia)
> Dominant acid is sulfuric, but source is biological, not industrial (tested with isotope studies).

The Sulfur Cycle

<u>Major emitted compounds</u>

- Sulfur dioxide (SO_2): volcanos, fumaroles, etc.; *fossil fuel burning*

- Hydrogen sulfide (H_2S): biogenic emissions from anoxic soils and waters

- Carbonyl sulfide (OCS): oceanic biology; *industrial by-product*

- Dimethyl sulfide (($CH_3)_2S$): oceanic biology

The Natural Sulfur Cycle - Schematically
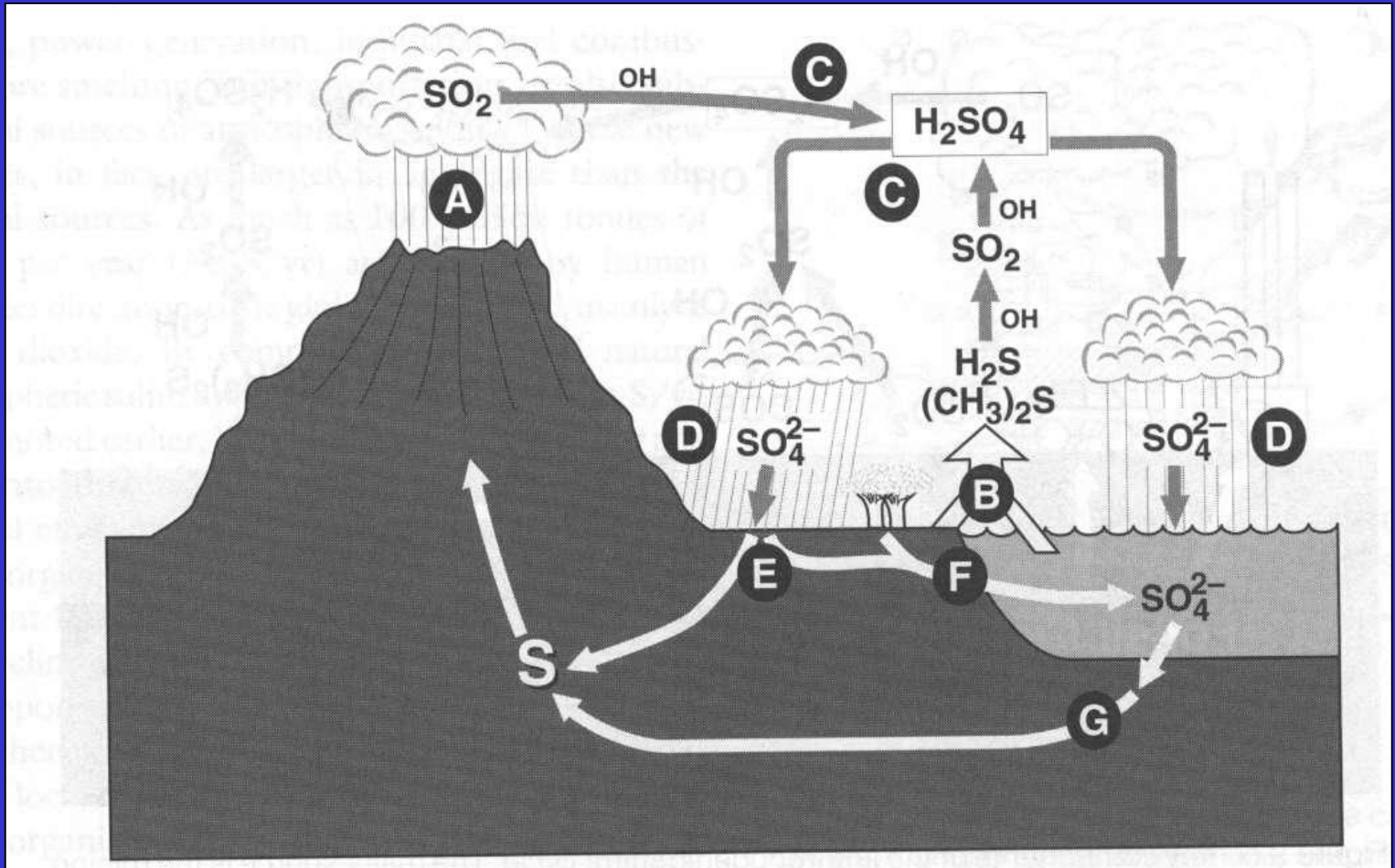
Reservoirs and Fluxes
(We'll look at these 'box diagrams' in detail next week)
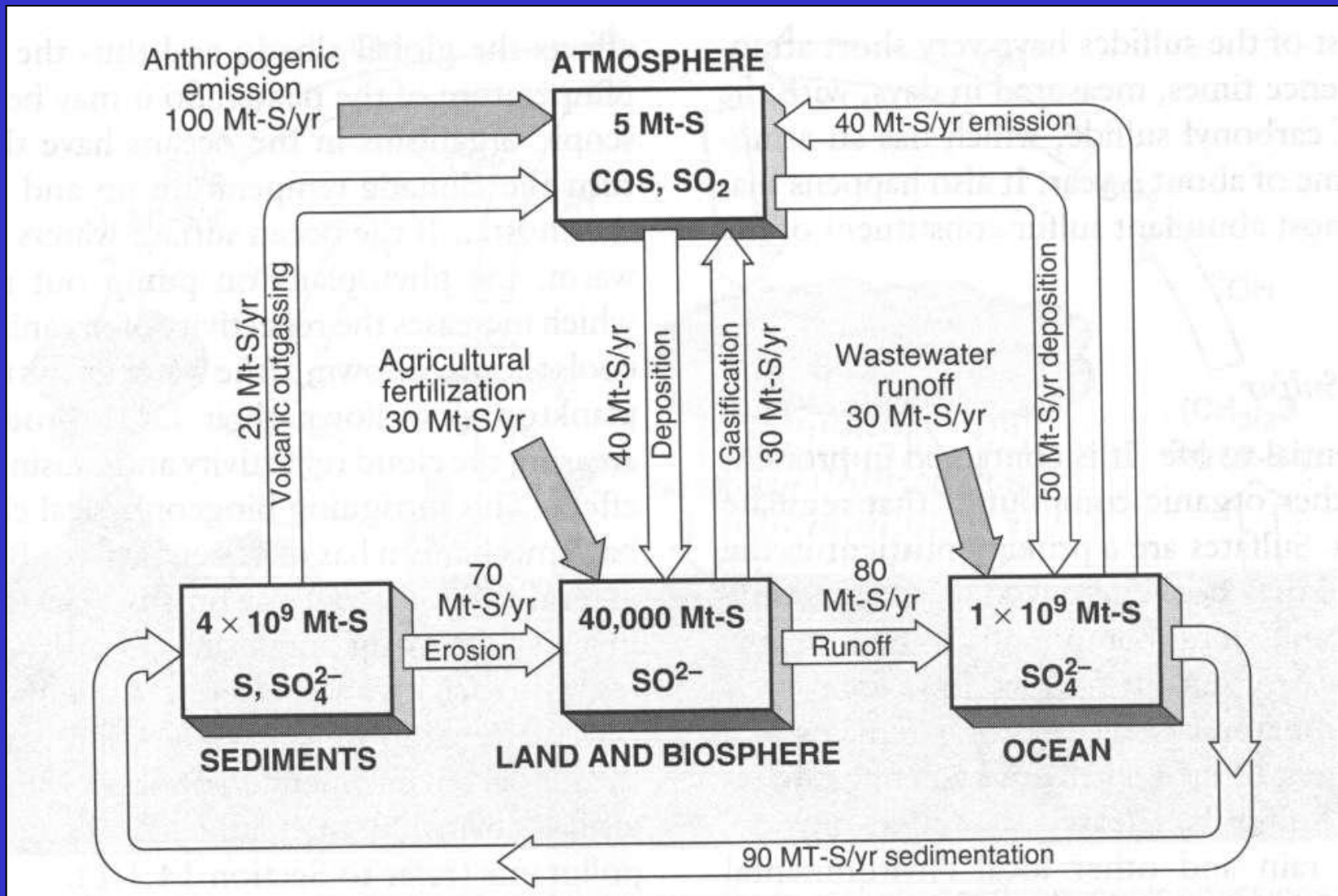
Magnitudes

1 tonne (metric ton) = 1000 kg = 1×10^6 g
1 Megatonne (Mt) = 1×10^6 tonne = 1×10^{12} g
1 Gigatonne (Gt) = 1×10^9 tonne = 1×10^{15} g
1 Teragram (Tg) = 1×10^{12} g

Natural sources:	90 Mt S
Anthropogenic sources:	100 Mt S
Sinks:	190 Mt S

Anthropogenic Components and Fluxes

Sulfate Ion Concentrations 1985-2003

1984 **1985** 1986

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

1985 **1986** 1987

SO$_4^{-2}$ (mg/L)

- ≤ 0.50
- 0.50 - 0.75
- 0.75 - 1.00
- 1.00 - 1.25
- 1.25 - 1.50
- 1.50 - 1.75
- 1.75 - 2.00
- 2.00 - 2.25
- 2.25 - 2.50
- 2.50 - 2.75
- 2.75 - 3.00
- > 3.00

Sulfate Ion Concentrations
1985-2003

1986 **1987** 1988

SO$_4^{-2}$ (mg/L)

≤ 0.50	
0.50 - 0.75	
0.75 - 1.00	
1.00 - 1.25	
1.25 - 1.50	
1.50 - 1.75	
1.75 - 2.00	
2.00 - 2.25	
2.25 - 2.50	
2.50 - 2.75	
2.75 - 3.00	
> 3.00	

Sulfate Ion Concentrations 1985-2003

1987 **1988** 1989

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

1988 **1989** 1990

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations
1985-2003

1989 **1990** 1991

SO$_4^{-2}$ (mg/L)

≤ 0.50	
0.50 - 0.75	
0.75 - 1.00	
1.00 - 1.25	
1.25 - 1.50	
1.50 - 1.75	
1.75 - 2.00	
2.00 - 2.25	
2.25 - 2.50	
2.50 - 2.75	
2.75 - 3.00	
> 3.00	

Sulfate Ion Concentrations 1985-2003

SO$_4^{-2}$ (mg/L)

≤ 0.50	
0.50 - 0.75	
0.75 - 1.00	
1.00 - 1.25	
1.25 - 1.50	
1.50 - 1.75	
1.75 - 2.00	
2.00 - 2.25	
2.25 - 2.50	
2.50 - 2.75	
2.75 - 3.00	
> 3.00	

1990 **1991** 1992

Sulfate Ion Concentrations 1985-2003

1991 **1992** 1993

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

1992 **1993** 1994

SO$_4^{-2}$ (mg/L)

- ≤ 0.50
- 0.50 - 0.75
- 0.75 - 1.00
- 1.00 - 1.25
- 1.25 - 1.50
- 1.50 - 1.75
- 1.75 - 2.00
- 2.00 - 2.25
- 2.25 - 2.50
- 2.50 - 2.75
- 2.75 - 3.00
- > 3.00

Sulfate Ion Concentrations 1985-2003

1993 **1994** 1995

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

1994 **1995** 1996

SO$_4^{-2}$ (mg/L)

≤ 0.50	
0.50 - 0.75	
0.75 - 1.00	
1.00 - 1.25	
1.25 - 1.50	
1.50 - 1.75	
1.75 - 2.00	
2.00 - 2.25	
2.25 - 2.50	
2.50 - 2.75	
2.75 - 3.00	
> 3.00	

Sulfate Ion Concentrations 1985-2003

1995 **1996** 1997

SO$_4^{-2}$ (mg/L)

- ≤ 0.50
- 0.50 - 0.75
- 0.75 - 1.00
- 1.00 - 1.25
- 1.25 - 1.50
- 1.50 - 1.75
- 1.75 - 2.00
- 2.00 - 2.25
- 2.25 - 2.50
- 2.50 - 2.75
- 2.75 - 3.00
- > 3.00

Sulfate Ion Concentrations 1985-2003

1996 **1997** 1998

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

1997 **1998** 1999

SO_4^{-2} (mg/L)

- ≤ 0.50
- 0.50 - 0.75
- 0.75 - 1.00
- 1.00 - 1.25
- 1.25 - 1.50
- 1.50 - 1.75
- 1.75 - 2.00
- 2.00 - 2.25
- 2.25 - 2.50
- 2.50 - 2.75
- 2.75 - 3.00
- > 3.00

Sulfate Ion Concentrations 1985-2003

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

1998 **1999** 2000

Sulfate Ion Concentrations 1985-2003

1999 **2000** 2001

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

Sulfate Ion Concentrations 1985-2003

2001 **2002** 2003

SO$_4^{-2}$ (mg/L)

≤ 0.50
0.50 - 0.75
0.75 - 1.00
1.00 - 1.25
1.25 - 1.50
1.50 - 1.75
1.75 - 2.00
2.00 - 2.25
2.25 - 2.50
2.50 - 2.75
2.75 - 3.00
> 3.00

Sulfate Ion Concentrations 1985-2003

SO$_4^{-2}$ (mg/L)

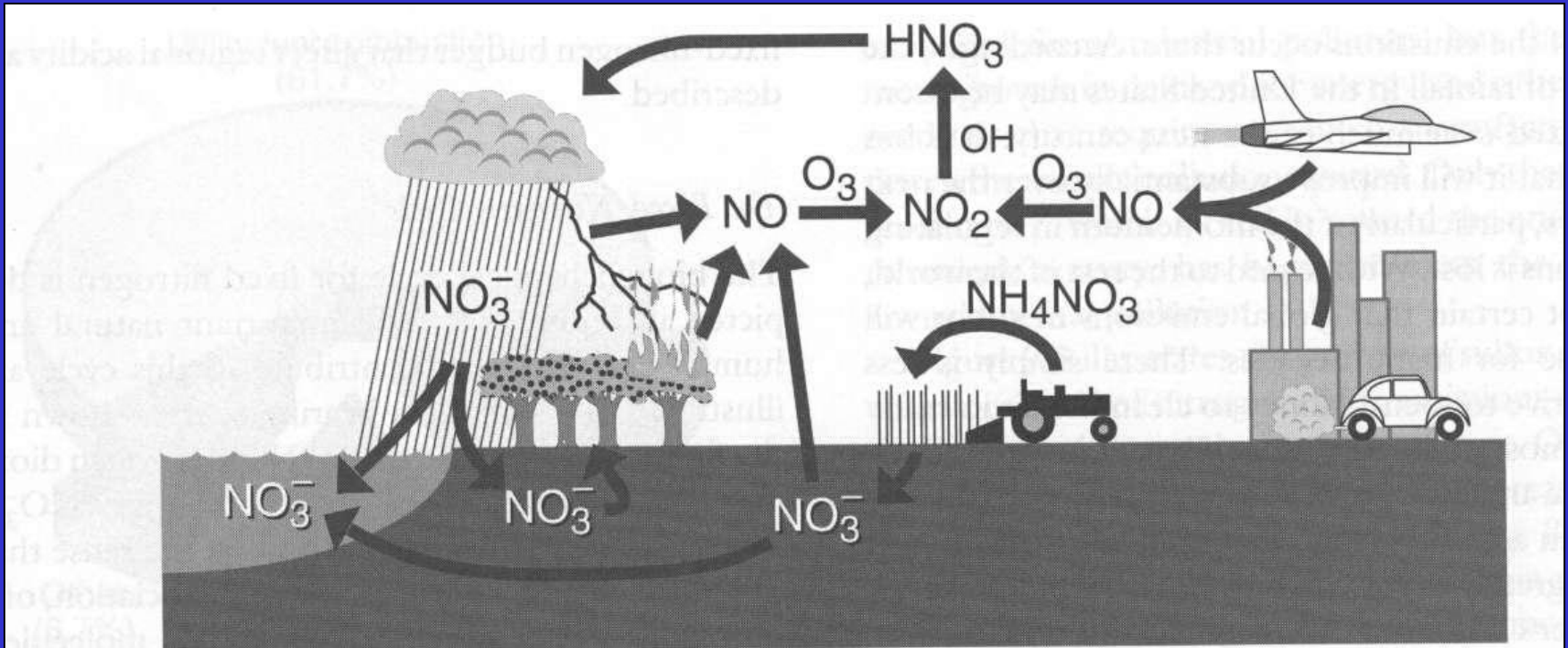|	
≤ 0.50	
0.50 - 0.75	
0.75 - 1.00	
1.00 - 1.25	
1.25 - 1.50	
1.50 - 1.75	
1.75 - 2.00	
2.00 - 2.25	
2.25 - 2.50	
2.50 - 2.75	
2.75 - 3.00	
> 3.00	

2002 **2003** 2004
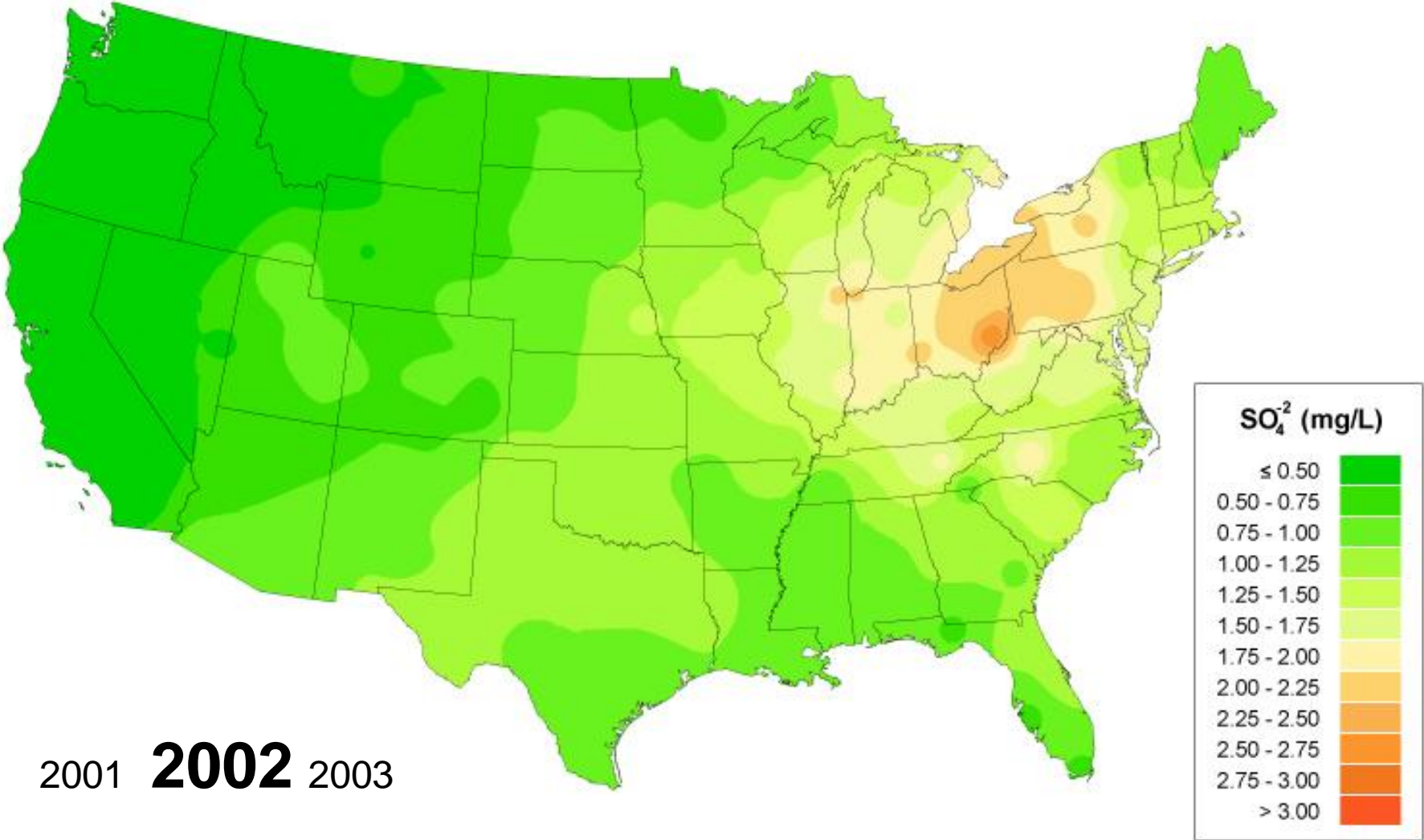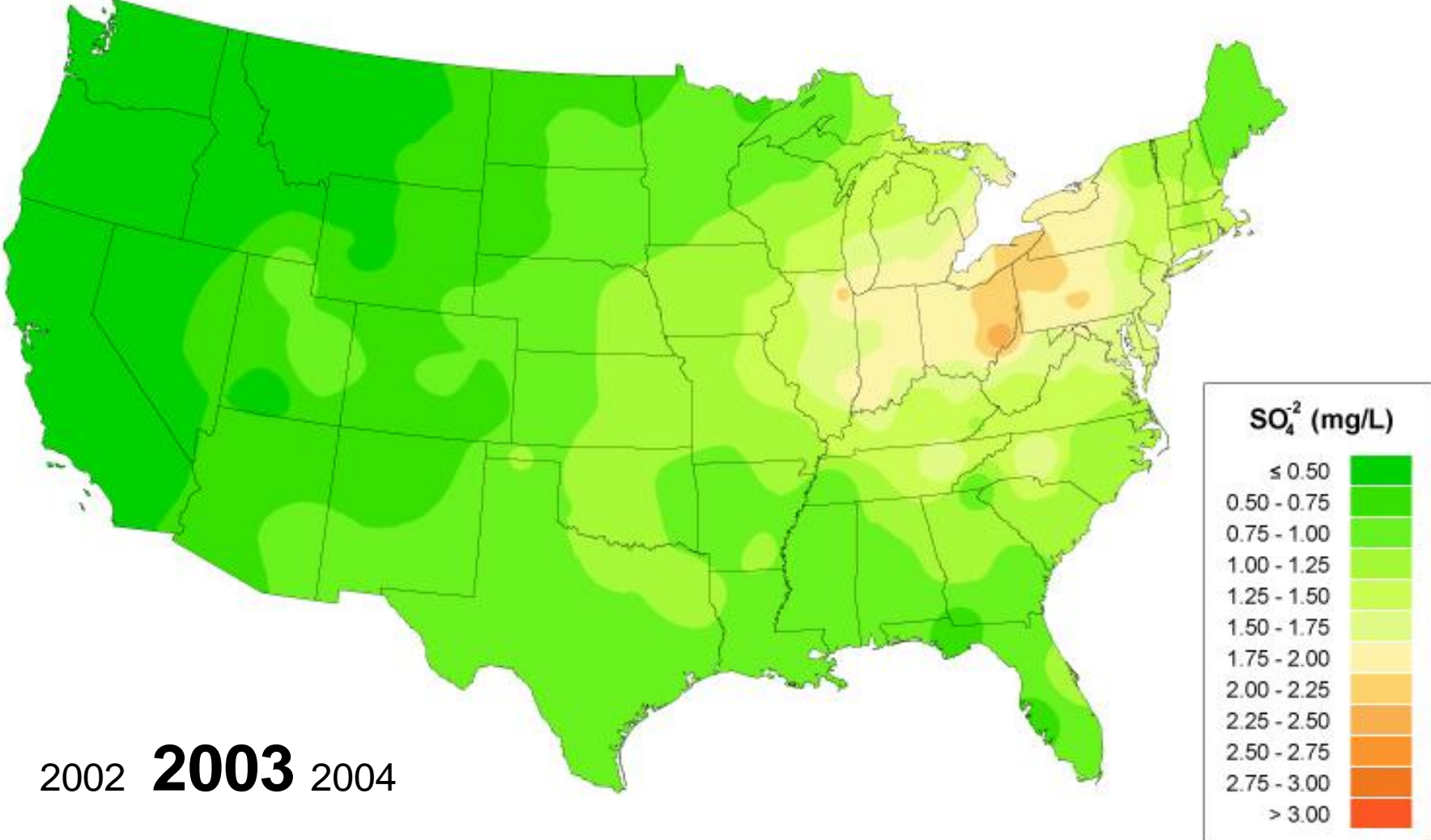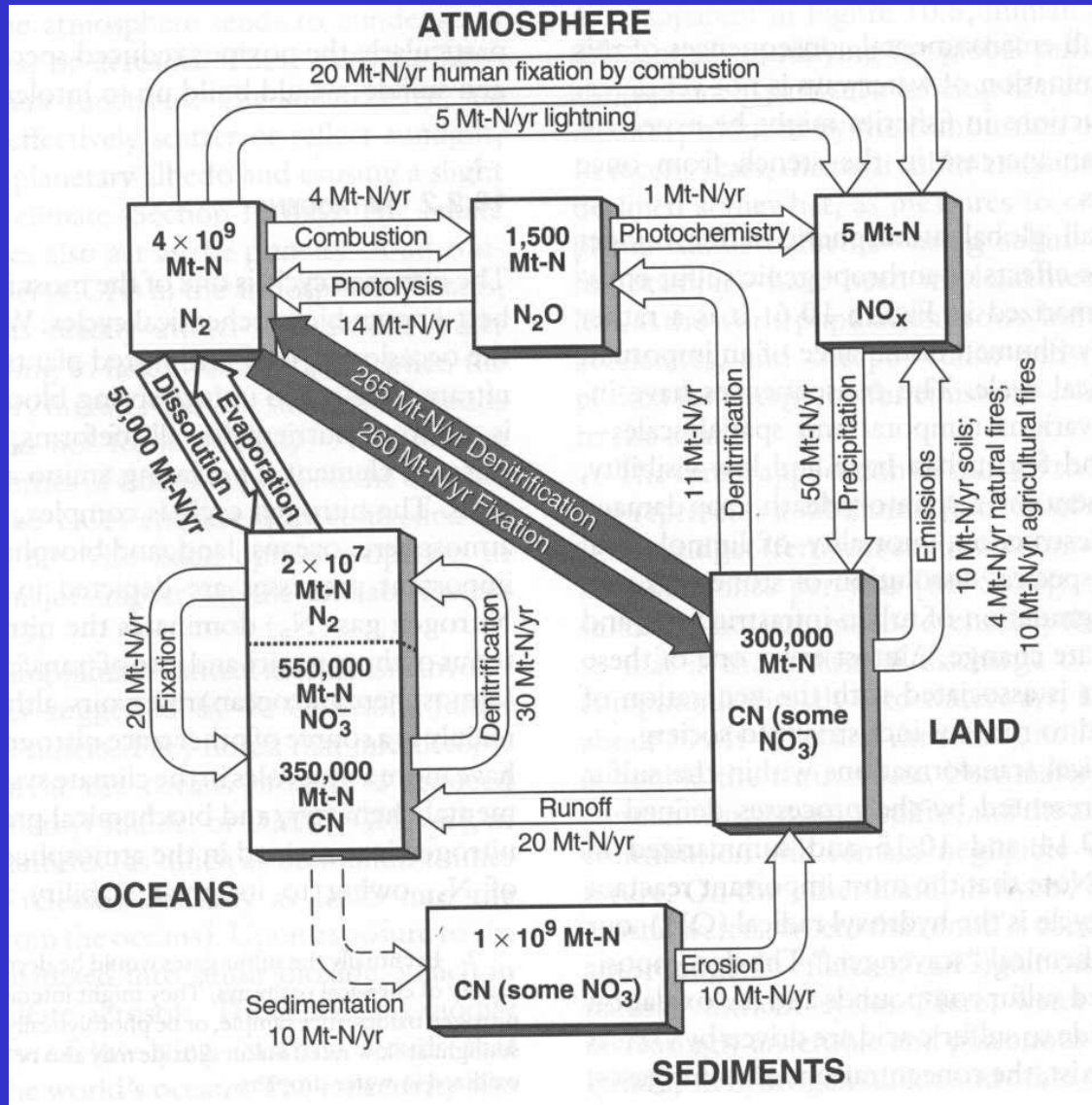
The Nitrogen Cycle

<u>Major emitted compounds</u>
- Nitrous oxide (N_2O): denitrifying bacteria in soils; *industry*
- Nitric oxide (NO): soils, biomass burning; *combustion*
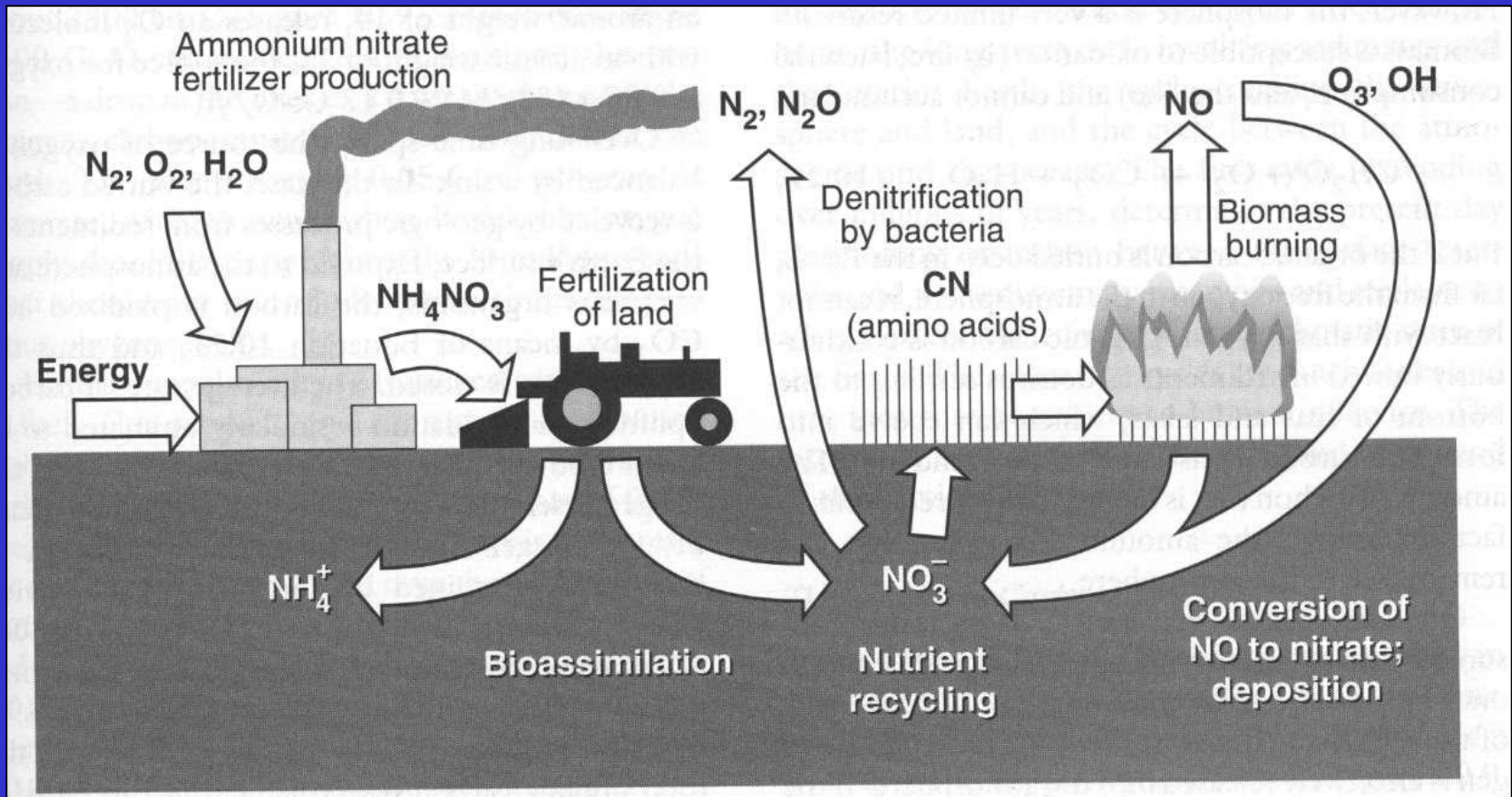- Ammonia (NH_3): decay processes; *fertilizers, animal wastes*

Natural: ~ 20 Mt N yr^{-1}
Anthropogenic: ~ 30 Mt N yr^{-1}

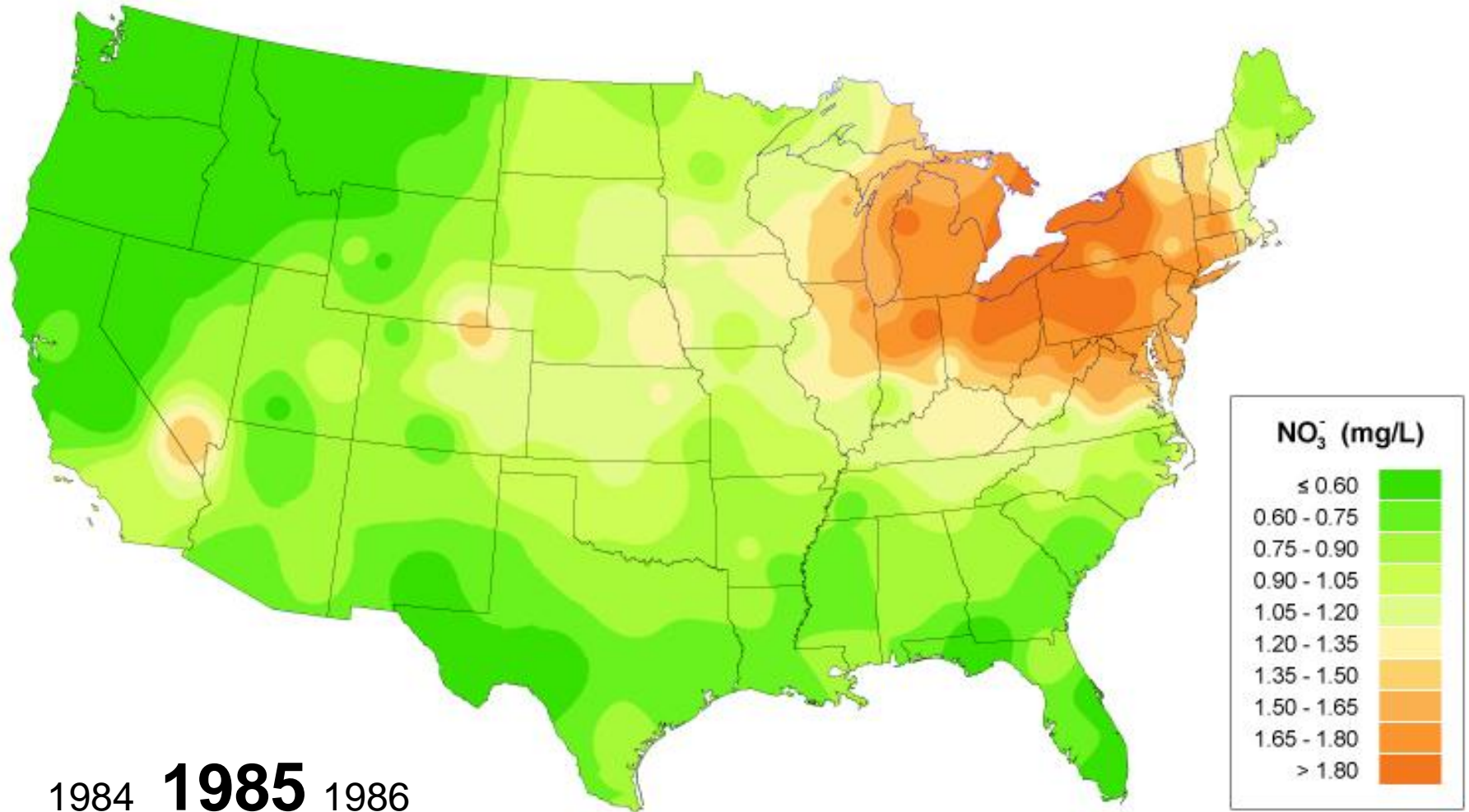# Anthropogenic components
(fertilizer-related)

Natural: ~ 20 Mt N yr^{-1}

Anthropogenic: ~ 30 Mt N yr^{-1}

Nitrate Ion Concentrations 1985-2003

NO$_3^-$ (mg/L)

≤ 0.60	
0.60 - 0.75	
0.75 - 0.90	
0.90 - 1.05	
1.05 - 1.20	
1.20 - 1.35	
1.35 - 1.50	
1.50 - 1.65	
1.65 - 1.80	
> 1.80	

1984 **1985** 1986

Nitrate Ion Concentrations
1985-2003

NO$_3^-$ (mg/L)

≤ 0.60
0.60 - 0.75
0.75 - 0.90
0.90 - 1.05
1.05 - 1.20
1.20 - 1.35
1.35 - 1.50
1.50 - 1.65
1.65 - 1.80
> 1.80

1985 **1986** 1987

Nitrate Ion Concentrations 1985-2003

NO$_3^-$ (mg/L)

- ≤ 0.60
- 0.60 - 0.75
- 0.75 - 0.90
- 0.90 - 1.05
- 1.05 - 1.20
- 1.20 - 1.35
- 1.35 - 1.50
- 1.50 - 1.65
- 1.65 - 1.80
- > 1.80

1986 **1987** 1988

Nitrate Ion Concentrations 1985-2003

1987 **1988** 1989

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**Nitrate Ion Concentrations
1985-2003**

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Nitrate Ion Concentrations 1985-2003

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Nitrate Ion Concentrations 1985-2003

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1990 **1991** 1992

Nitrate Ion Concentrations 1985-2003

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1991 **1992** 1993

Nitrate Ion Concentrations 1985-2003

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1992 **1993** 1994

Nitrate Ion Concentrations 1985-2003

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1993 **1994** 1995

Nitrate Ion Concentrations
1985-2003

1994 **1995** 1996

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Nitrate Ion Concentrations 1985-2003

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1995 **1996** 1997

Nitrate Ion Concentrations 1985-2003

1996 **1997** 1998

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Nitrate Ion Concentrations 1985-2003

Nitrate Ion Concentrations 1985-2003

1998 **1999** 2000

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Nitrate Ion Concentrations 1985-2003

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1999 **2000** 2001

Nitrate Ion Concentrations
1985-2003

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2000 **2001** 2002

Nitrate Ion Concentrations 1985-2003

2001 **2002** 2003

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Nitrate Ion Concentrations 1985-2003

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2002 **2003** 2004

Ammonium Ion Concentrations
1985-2003

1984 **1985** 1986

NH$_4^+$ (mg/L)

- ≤ 0.10
- 0.10 - 0.15
- 0.15 - 0.20
- 0.20 - 0.25
- 0.25 - 0.30
- 0.30 - 0.35
- 0.35 - 0.40
- 0.40 - 0.45
- 0.45 - 0.50
- 0.50 - 0.55
- > 0.55

Ammonium Ion Concentrations 1985-2003

1985 **1986** 1987

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Ammonium Ion Concentrations
1985-2003

1986 **1987** 1988

NH₄⁺ (mg/L)

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Ammonium Ion Concentrations
1985-2003

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**Ammonium Ion Concentrations
1985-2003**

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Ammonium Ion Concentrations
1985-2003

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Ammonium Ion Concentrations
1985-2003

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**Ammonium Ion Concentrations
1985-2003**

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Ammonium Ion Concentrations 1985-2003

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Ammonium Ion Concentrations 1985-2003

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Ammonium Ion Concentrations
1985-2003

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Ammonium Ion Concentrations 1985-2003

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Ammonium Ion Concentrations 1985-2003

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Ammonium Ion Concentrations 1985-2003

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Ammonium Ion Concentrations
1985-2003

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1999 **2000** 2001

Ammonium Ion Concentrations 1985-2003

2000 **2001** 2002

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Ammonium Ion Concentrations 1985-2003

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2001 **2002** 2003

Ammonium Ion Concentrations 1985-2003

2002 **2003** 2004

NH$_4^+$ (mg/L)

≤ 0.10
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Types of Environmental Damage

- Focus today on plants and animals.

- First signs of acid-related damage came as "fish kills" in Scandinavian lakes.

- Many regions show forest deaths (Germany, NE US), but hard to separate conclusively from other pollutant causes.

Trees and other plants

Affected in two ways:
- Direct (primary) deposition – burning of leaves, etc.
- Secondary effects – related to reactions in soil and forest litter; alters nutrients

Possible Mechanisms
1. Reacts with minerals to leach out some metals, such as Al, which can be toxic to plants.
2. Changes nutrients available to plants
3. Affects decomposition of humus and subsequent organic material
4. Otherwise disturbs plant physiology

Aquatic Life

- Acid or acid-created byproduct arrives by direct deposition or via runoff

- pH changes in many lakes have been observed

- Fish are very sensitive to acidity, particularly in the egg and larval stages.

- Some fish lose reproductive capacities under acidic conditions (salmon, trout at pH < 5.5; most others at pH < 4.2; "dead lakes" at pH ~ 3.5)

- Mountain lakes and rivers often have seasonally-varying losses due to melting of acidic snows in the spring – gives rise to a "burst" of highly acidic water.
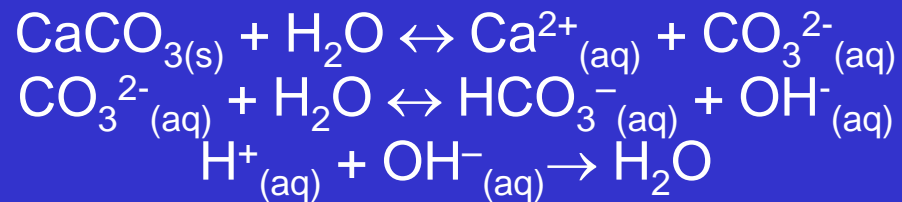
Susceptibility to acidity

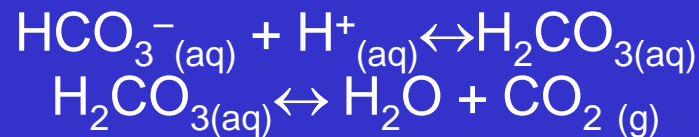|	pH 6.5	pH 6.0	pH 5.5	pH 5.0	pH 4.5	pH 4.0
TROUT	■	■	■	■		
BASS	■	■	■			
PERCH	■	■	■	■	■	
FROGS	■	■	■	■	■	■
SALAMANDERS	■	■	■	■		
CLAMS	■	■				
CRAYFISH	■	■	■			
SNAILS	■	■				
MAYFLY	■	■	■			

The Role of Soils

<u>What is a *buffer*?</u>
Something that acts to mitigate the effects on pH of acid or base addition
In the laboratory, usually a solution of a weak acid and its conjugate base
(or vice versa). In natural systems, the buffering capacity comes from
minerals in the soils, to varying degrees. Of particular importance are
carbonates (CO_3^{2-}), such as limestone ($CaCO_3$).

$$CaCO_{3(s)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)}$$
$$CO_3^{2-}_{(aq)} + H_2O \leftrightarrow HCO_3^-_{(aq)} + OH^-_{(aq)}$$
$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O$$

If enough H^+ is added, CO_2 can be released:

$$HCO_3^-_{(aq)} + H^+_{(aq)} \leftrightarrow H_2CO_{3(aq)}$$
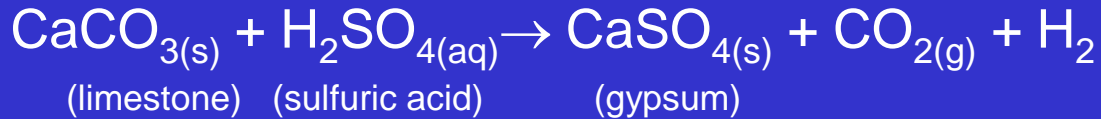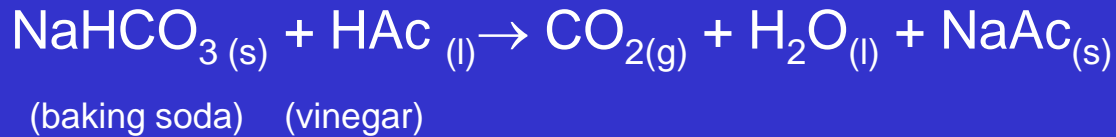$$H_2CO_{3(aq)} \leftrightarrow H_2O + CO_{2\ (g)}$$

This set of reactions can effectively buffer pH's from the mid-5's to about
8.3. At lower pH's other mineral systems are involved – silicates,
aluminum ions, iron ions.

Effects on Structures

Stonework and statuary

• Many buildings and monuments are made of limestone ($CaCO_3$) or marble, which is the metamorphic version of limestone.

• Add acidic precipitation. Result? Similar to the kid's volcano made of baking soda and vinegar

$$NaHCO_{3\,(s)} + HAc_{(l)} \rightarrow CO_{2(g)} + H_2O_{(l)} + NaAc_{(s)}$$

(baking soda)   (vinegar)

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + CO_{2(g)} + H_2$$

(limestone)   (sulfuric acid)   (gypsum)

• Gypsum is the mineral used to make dry-wall materials and plasters; it is a white powdery substance.

• These chemical processes cause degradation of statues, building facades, gravestones, etc. Average rate of degradation for marble is about 10 μm/m rainfall.

Other Materials

• Metals: Zinc, copper and steel all susceptible to dissolution by acids, mainly by sulfuric acid.

• Paints: Easily etched by acids; car finishes especially vulnerable

Strategies for Remediation

- Reducing emissions that lead to acid precipitation
- Use low-sulfur fuels in sensitive areas
- Remove sulfur from high-sulfur fuels before burning them
- "Scrub" the emissions from fuel-burning plants
- Disperse emissions using higher smokestacks
- Develop alternative energy sources
- Site power plants to minimize local impact
- Try to counteract effects of acidification by adding limestone to bodies of water

$$CaCO_{3(s)} + H_2O \leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)}$$
$$CO_3^{2-}_{(aq)} + H_2O \leftrightarrow HCO_3^-_{(aq)} + OH^-_{(aq)}$$
$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O$$