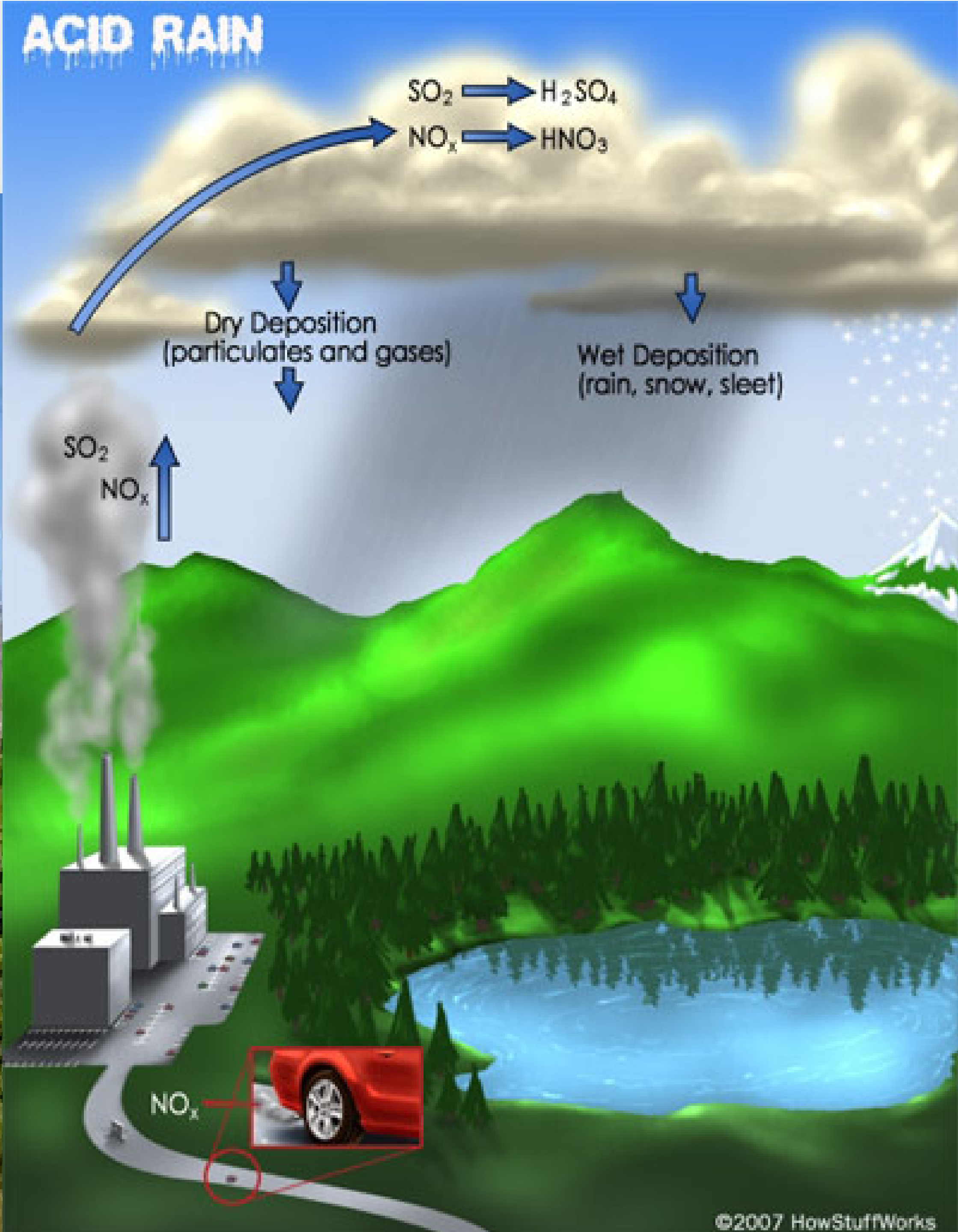
Acid Rain



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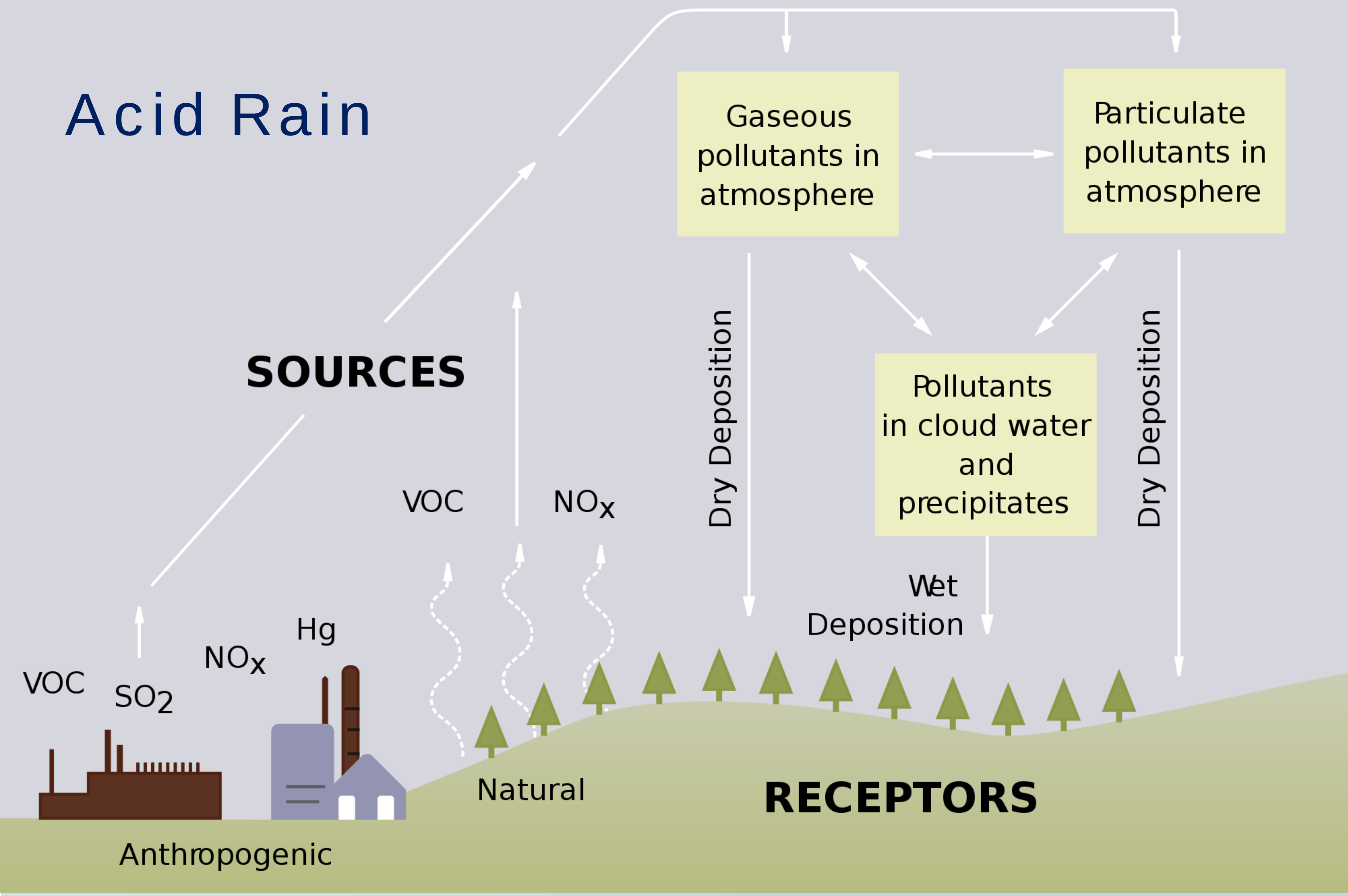
Acid Rain


Gaseous pollutants in atmosphere
Particulate pollutants in atmosphere
SOURCES
Dry Deposition
Pollutants in cloud water and precipitates
Dry Deposition
VOC
NO_x
Wet Deposition
Hg
NO_x
VOC
SO_2
Natural
RECEPTORS
Anthropogenic

Acid Rain

- What is acid rain?
- Types of acid involved
- Acid rain precursors
- Transport and conversion of precursors
- pH of precipitation
- Biological effects
- Alkalinity
- Mitigation methods/technology
- Acid rain policy

Acid Deposition

Wet Deposition (acid rain, snow)

- Easy to measure; about half of acid deposition
- First measured in 1852 in England
- No widespread attention until 1961, when Swedish scientists hypothesized that declining fish populations (and, later, forest damage) might be caused by acid rain from coal-burning regions of Europe.
- By 1980, recognized as a major environmental problem in industrialized countries.

Acid Deposition

Dry deposition (acid gases and aerosols)

- Difficult to measure; importance recognized only in 1980s
- Main form of acid deposition near source
- Main cause of damage to foliage?

Droplet deposition (acid fogs)

- Generally less important than wet and dry deposition, except in certain locations
- Highest measured acidities, but total dose small

Acids and Acid Precursors

- Sulfur dioxide (SO_2) → sulfuric acid (H_2SO_4)
  - primarily from coal burning and smelting
- Nitrogen oxides (NO, NO_2) → nitric acid (HNO_3)
  - primarily from high-temperature combustion
- Formic and acetic acids (HCO_2H, CH_3CO_2H)
  - primarily from biomass burning, mostly in Africa and South America
- Carbonic acid ($CO_2 \rightarrow H_2CO_3$)
  - from CO_2 in atmosphere, responsible for acidity of pristine precipitation

strong acids

weak acids

Sources of Sulfur Dioxide (SO_2)

Anthropogenic

- 60-100 Mt(S)/y emitted into atmosphere worldwide
- US emissions: 32 Mt/y(1973) → 9.5 (2006) Mt/y SO_2
  - Coal-burning in power plants
  - Oil-burning (vehicles)
  - Industrial (smelting, etc.); responsible for intense local damage
- Biomass burning: 1-6 Mt(S)/y worldwide

Natural

- volcanoes (6-20 Mt(S)/y as SO_2)

1 Mt(S) = 2 Mt(SO_2) = 3 Mt(SO_4^{2-})

- Atomic mass of O = 16 g/mol
- Atomic mass of S = 32 g/mol
- Molecular mass of SO_2 = 64 g/mol
- Formula mass SO_4^{2-} = 96 g/mol

SO_2 to Acid

- In water solution, sulfur dioxide dissolves in water to form sulfurous acid, which can go on to form sulfuric acid.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$$

- In the gas phase, sulfur dioxide can form sulfuric acid, H_2SO_4.

$$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$$

$$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

Sulfurous and Sulfuric Acid Ionizations

- Sulfuric acid and sulfurous acid form hydronium ions

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

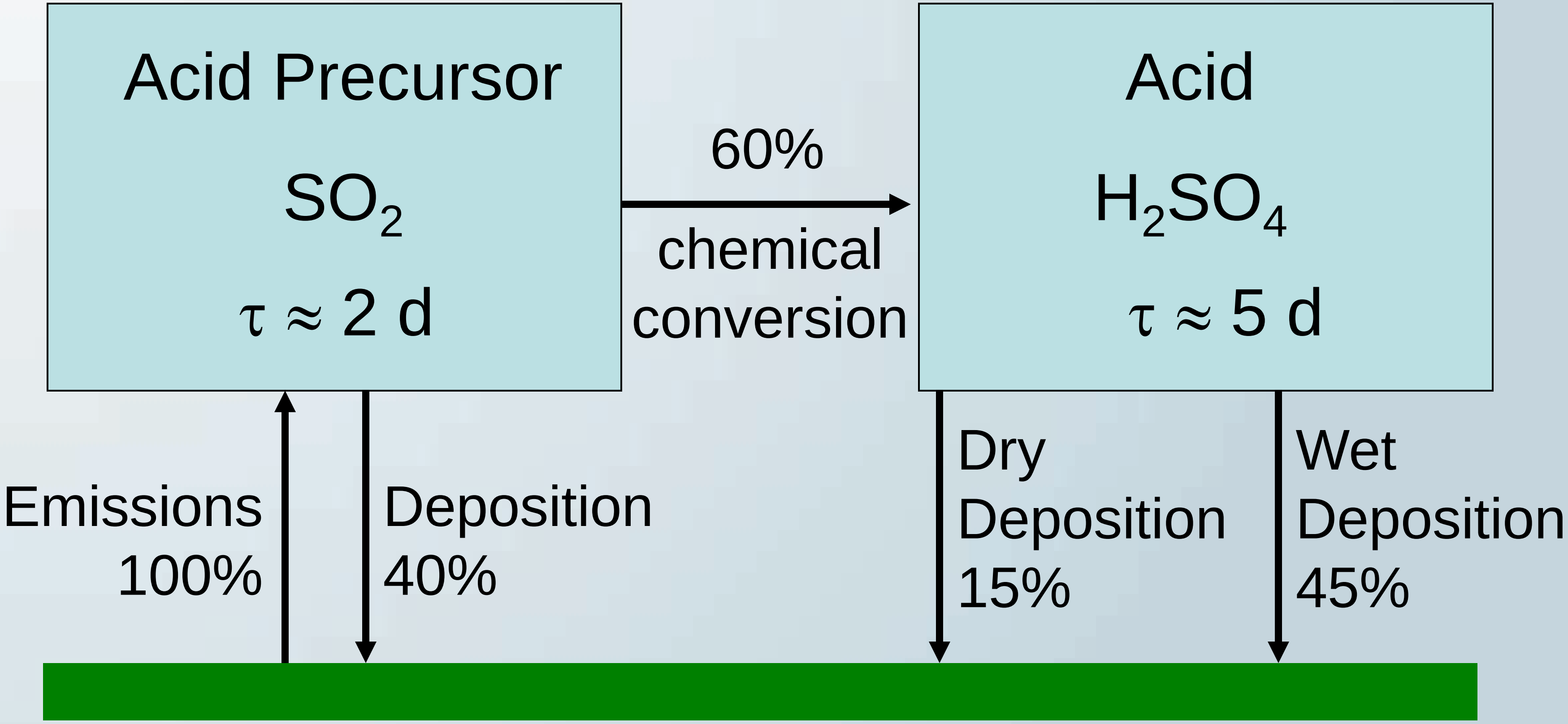
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$$

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$$

- The pH can drop to 4.3 or lower.

Global Sulfur Budget



Acid Precursor

SO_2

$\tau \approx 2$ d

60%

chemical conversion

Acid

H_2SO_4

$\tau \approx 5$ d

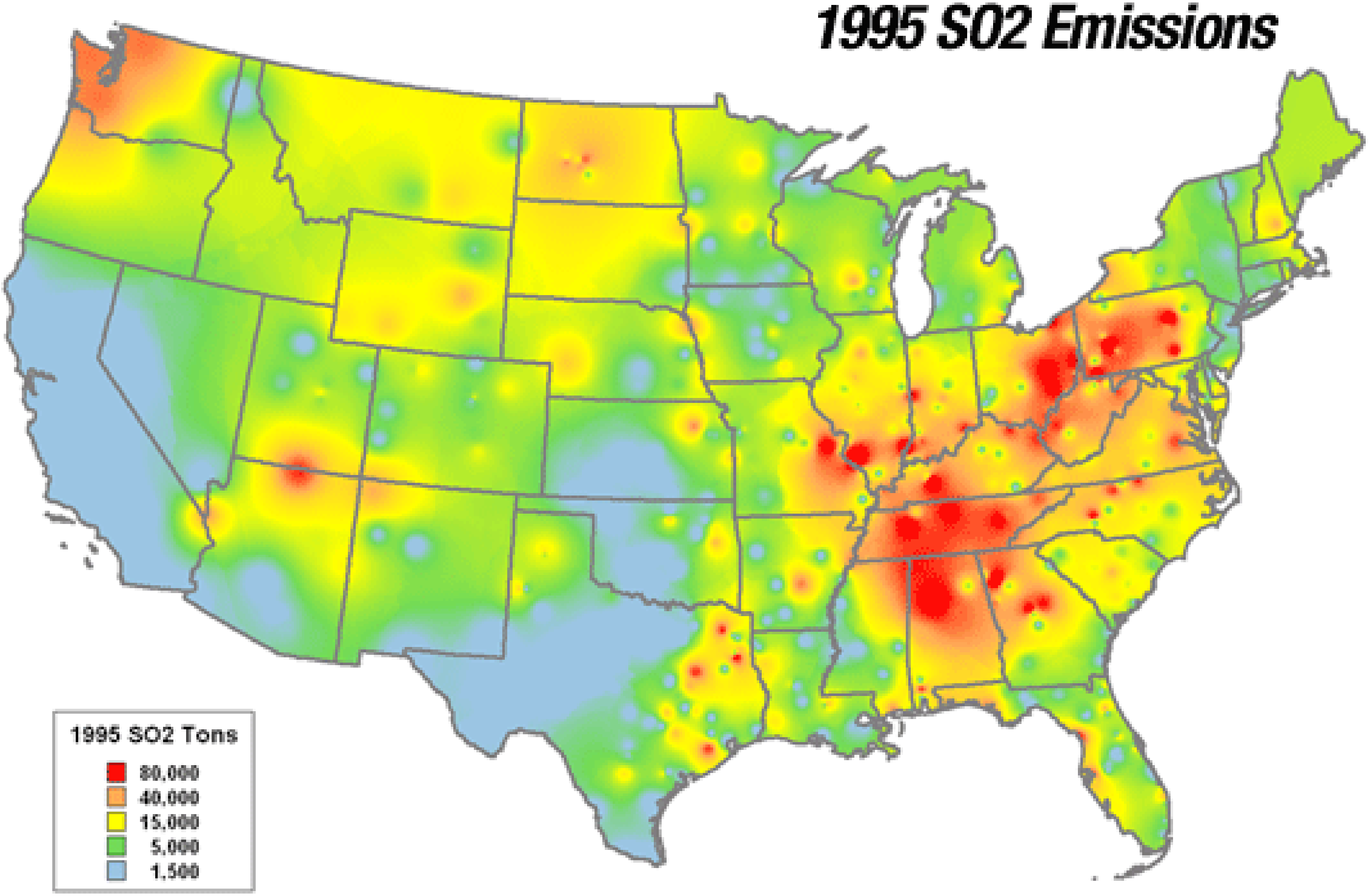
Emissions 100%

Deposition 40%

Dry Deposition 15%

Wet Deposition 45%

1995 SO2 Emissions



Average density of coal use in the US, western Europe, and China is ≈ 100 t/km^2/y; in high-use areas, >300 t/km^2/y

Region	Coal Use 1990, (Mt)	Area (10^6 km^2)	Density (t/km^2)	2003
United States	784	7.672	102	120
New England	7.8	0.163	48	
Middle Atlantic	80	0.258	308	
EN Central	204	0.632	322	
WN Central	77	1.316	59	
South Atlantic	158	0.691	229	
ES Central	93	0.463	200	
WS Central	80	1.107	72	
Mountain	79	2.215	36	
Pacific	6.6	0.826	8.0	
Western Europe	400	4.375	91	70
France	24	0.547	44	
BeNeLux	33	0.029	1160	
Italy	21	0.301	68	
Spain	25	0.505	49	
Sweden	3.8	0.450	8.4	
Turkey	31	0.780	40	
United Kingdom	91	0.244	370	
West Germany	110	0.249	440	150

Coal Use and SO_2 Emissions

- In 1990, density of coal use in US, western Europe, and China averaged ≈100 $t/km^2/y$
- Sulfur content of US coal ranges from <0.5% to >7%; on average, ≈2.5% S
- Emission density: What is the emission density in $g(S)/m^2/y$?

$$\frac{?\ \mathrm{g\,S}}{\mathrm{m^2\,y}} = \frac{100\ \cancel{\mathrm{t\,coal}}}{\cancel{\mathrm{km^2}}\ \mathrm{y}}\left(\frac{2.5\,\cancel{\mathrm{t}}\,\mathrm{S}}{100\ \cancel{\mathrm{t\,coal}}}\right)\left(\frac{10^6\ \mathrm{g}}{1\ \cancel{\mathrm{t}}}\right)\left(\frac{1\ \cancel{\mathrm{km}}}{10^3\ \mathrm{m}}\right)^2 = 2.5\ \mathrm{g(S)/m^2y}$$

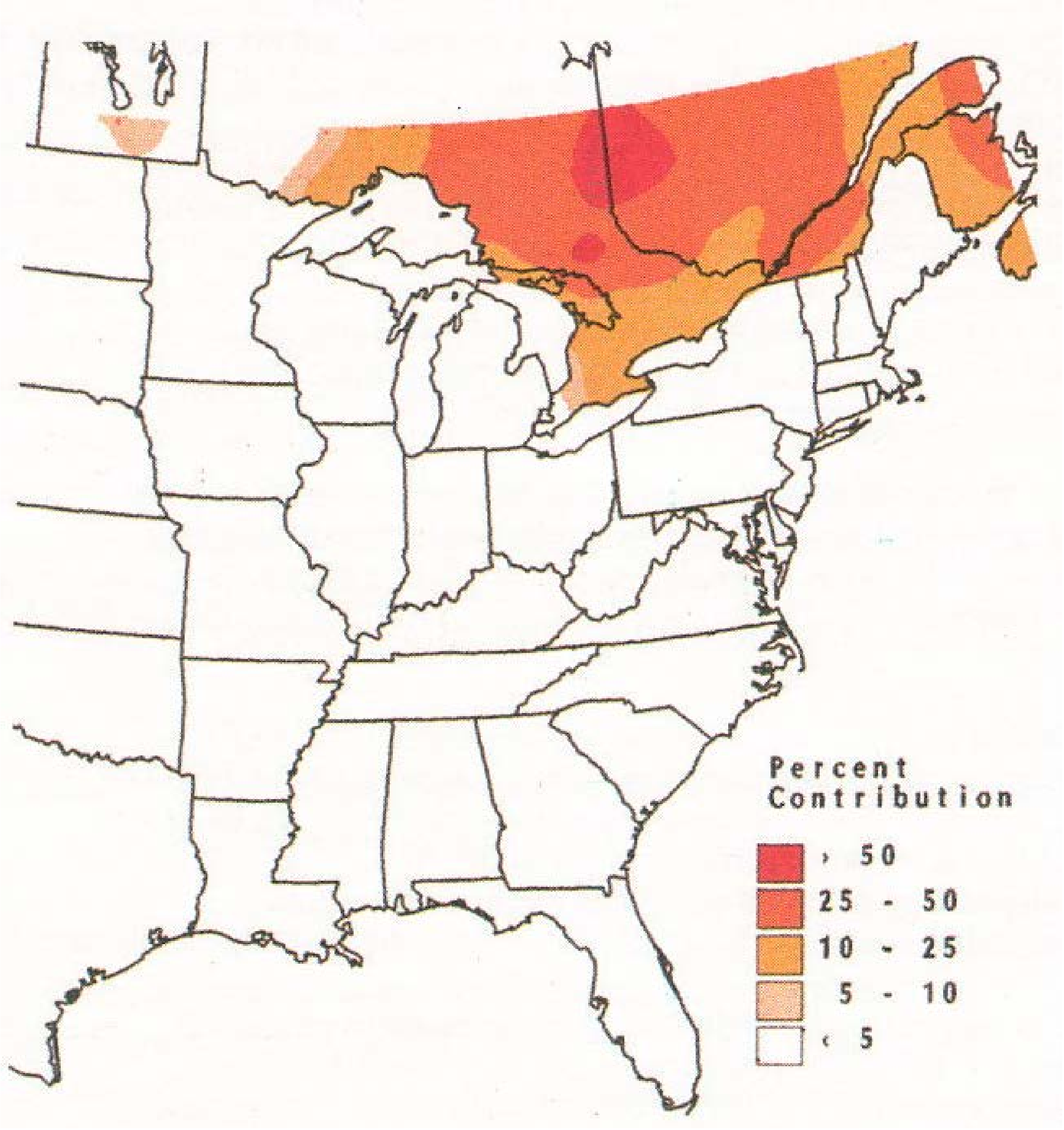
Emissions are 3+ times higher in high coal-use areas

Where SO_2 Emissions Deposited?

- Of SO_2 emitted in the Eastern US, ≈25% is converted into H_2SO_4, deposited in rain/snow
- The residence time for SO_2 is ≈4 days, so if the average wind velocity is 15 km/h, sulfate is deposited roughly 900 mi downwind of source.

$$? \text{ mi} = 4\,\cancel{\text{day}}\left(\frac{24\,\cancel{\text{h}}}{1\,\cancel{\text{day}}}\right)\left(\frac{15\,\cancel{\text{km}}}{1\,\cancel{\text{h}}}\right)\left(\frac{1\text{ mi}}{1.609\,\cancel{\text{km}}}\right) = 895\text{ mi} \approx 900\text{ mi}$$

Contribution of U.S. Emissions to Total S Deposition in Canada



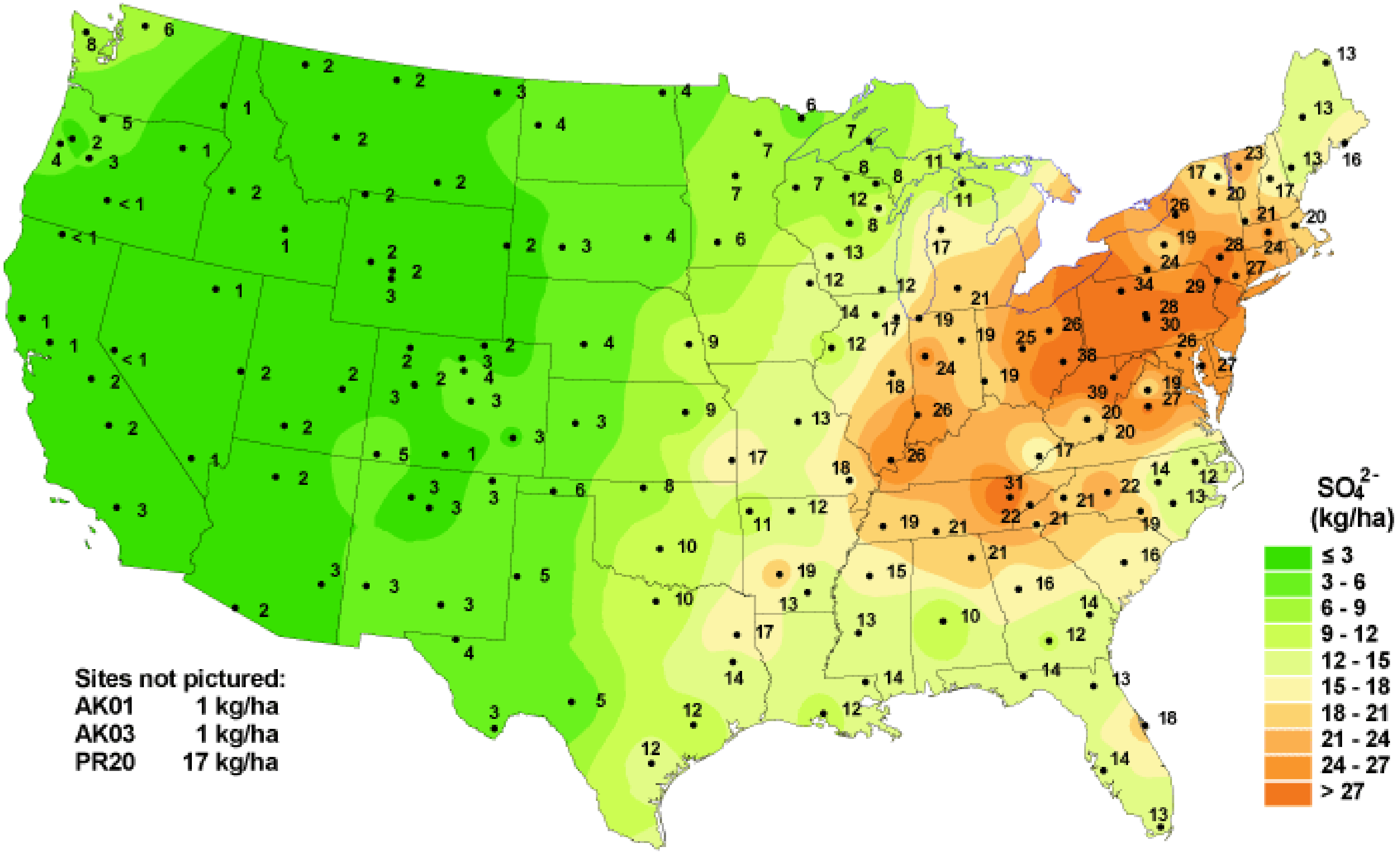
SO_2 Emissions and Wet Deposition

- If 25% of the SO_2 emissions ($\approx$2.5 g(S)/m^2/y) are deposited as H_2SO_4, then wet deposition downwind should average $\approx$0.6 g(S)/m^2/y as H_2SO_4. How many kilograms of sulfate. SO_4^{2-}, from the sulfuric acid are deposited per hectare per year?

$$\frac{?\ \text{kg SO}_4^{2-}}{\text{ha}\cdot\text{y}} = \frac{0.6\ \cancel{\text{g S}}}{\cancel{\text{m}^2}\ \text{y}}\left(\frac{1\ \cancel{\text{mol S}}}{32\ \cancel{\text{g S}}}\right)\left(\frac{1\ \cancel{\text{mol SO}_4^{2}}}{1\ \cancel{\text{mol S}}}\right)\left(\frac{96\ \cancel{\text{g}}\ \text{SO}_4^{2-}}{1\ \cancel{\text{mol SO}_4^{2-}}}\right)\left(\frac{10^4\ \cancel{\text{m}^2}}{1\ \text{ha}}\right)\left(\frac{1\ \text{kg}}{10^3\ \cancel{\text{g}}}\right)$$

$$= 18\ \text{kg SO}_4^{2-}/\text{ha}\cdot\text{y}$$

Wet Sulfate Deposition: 1994



Sites not pictured:

AK01	1 kg/ha
AK03	1 kg/ha
PR20	17 kg/ha

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

Wet Sulfate Deposition and pH

- H_2SO_4 is a “strong” acid with respect to the loss of the first H^+. But HSO_4^- is a weak acid.

  $$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

  $$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

  Every mole of H_2SO_4 produces about 1.01 moles of H^+.
- If the $[H^+]$ and pH of precipitation are primarily determined by the 0.6 g(S)/m^2/y deposited as H_2SO_4 in the ≈1 m/y of precipitation, what is the $[H^+]$ and pH of the rain?

$$\frac{?\ \text{mol H}^+}{\text{L}} = \frac{0.6\ \cancel{\text{g S}}}{\cancel{\text{m}^2}\ \cancel{\text{y}}}\left(\frac{1\ \cancel{\text{mol S}}}{32\ \cancel{\text{g S}}}\right)\left(\frac{1.01\ \text{mol H}^+}{1\ \cancel{\text{mol S}}}\right)\left(\frac{1\ \cancel{\text{y}}}{1\ \cancel{\text{m}}}\right)\left(\frac{1\ \cancel{\text{m}^3}}{10^3\ \text{L}}\right)$$

$$= 2 \times 10^{-5}\ \text{M H}^+$$

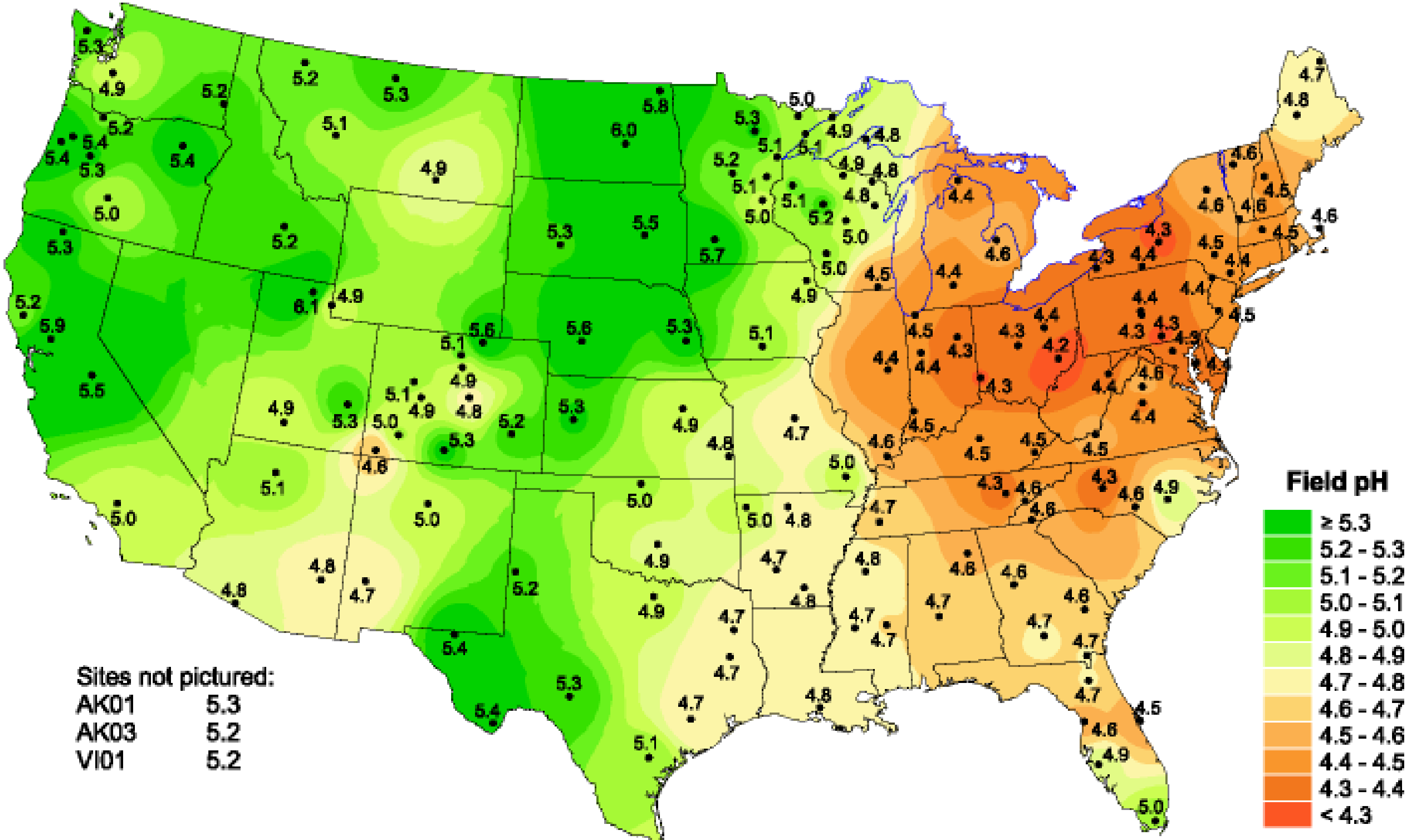
$$\text{pH} = -\log\,[\text{H}^+] = -\log 2 \times 10^{-5} = 4.7$$

A Simple Calculation

- There is a lot more going on here…details of emissions, transport, conversion, and deposition; deposition of other acids (e.g., HNO_3); acid-neutralizing reactions with gases (e.g., with NH_3) and aerosols ($CaCO_3$) …but this gives a feeling for the relationship between coal burning and the pH of rainfall
- Note:
  - If deposition rate is 2x higher, pH is 0.3 lower (pH = 4.4)
  - If deposition rate 2x lower, pH is 0.3 higher (pH=5.0)

Average pH of Rainfall: 1999

Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999



Sites not pictured:

AK01	5.3
AK03	5.2
VI01	5.2

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

Sources of Nitrogen Oxides (NOx)

Anthropogenic 30 Mt(N)/y global, 7 Mt(N)/y US

- Fossil-fuels (21 Mt(N)/y; 70% global, 90+% US)
  - vehicles (45% US)
  - power plants (35% US)
- Biomass burning (2-12 Mt(N)/y)
- Agricultural soils (0-4 Mt(N)/y)

Natural

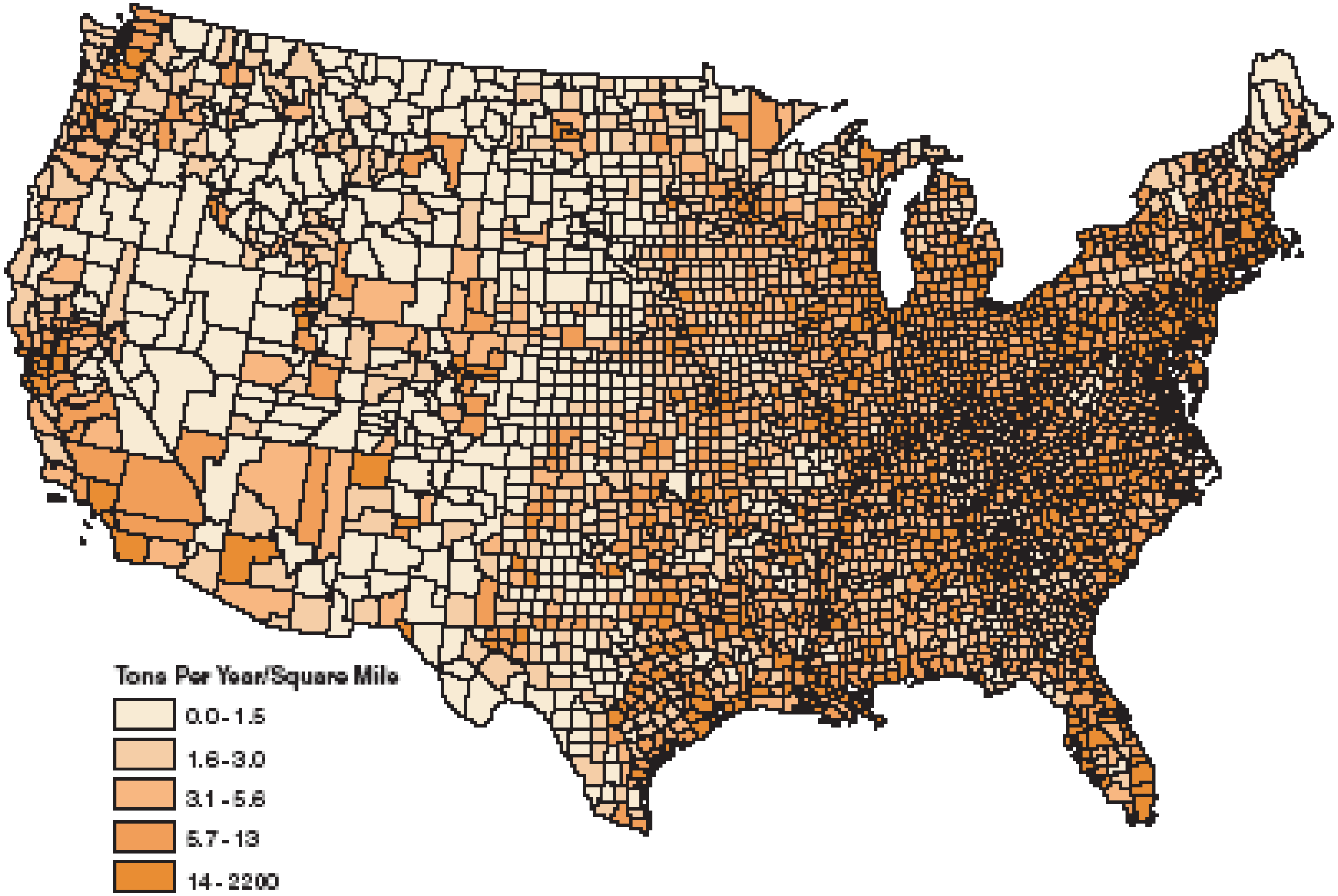
- Lightning (2-12 Mt(N)/y)
- Soils (3-8 Mt(N)/y)

NO_x is NO and NO_2

- Combustion and other high-temp processes in air (O_2 + N_2) produce NO and NO_2; together they are referred to as “nitrogen oxides” or “NOx”
- 95% of NOx from combustion sources is emitted in the form of NO, but this is quickly oxidized in the atmosphere to NO_2, and so emissions of NOx can be reported as t(NO_2).
- Using t(N) avoids the ambiguity.

$$1\ t(N) \times (46/14) = 3.3\ t(NO_2)$$

NO_2 Emission Density: 2001



$$\frac{?\ \mathrm{g(N)}}{\mathrm{m}^2\cdot\mathrm{y}} = \frac{14\ \cancel{\mathrm{ton}(\mathrm{NO_2})}}{\cancel{\mathrm{mi}^2}\cdot\mathrm{y}}\left(\frac{2000\ \cancel{\mathrm{lb}}}{1\ \cancel{\mathrm{ton}}}\right)\left(\frac{453.6\ \cancel{\mathrm{g}}}{1\ \cancel{\mathrm{lb}}}\right)\left(\frac{1\ \cancel{\mathrm{mi}}}{1.609\ \cancel{\mathrm{km}}}\right)^2\left(\frac{1\ \cancel{\mathrm{km}}}{10^3\ \mathrm{m}}\right)^2\left(\frac{14.0067\ \mathrm{g(N)}}{46.0055\ \cancel{\mathrm{g}(\mathrm{NO_2})}}\right)$$

$$= \mathbf{1.5\ g(N)/m^2\cdot y}$$

Nitric Acid Formation

- Nitric acid formation in gas phase

  $NO_2 + OH\cdot \rightarrow HNO_3$

- HNO_3 formation in water solution

  $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

- Nitrogen monoxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:

  $4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$

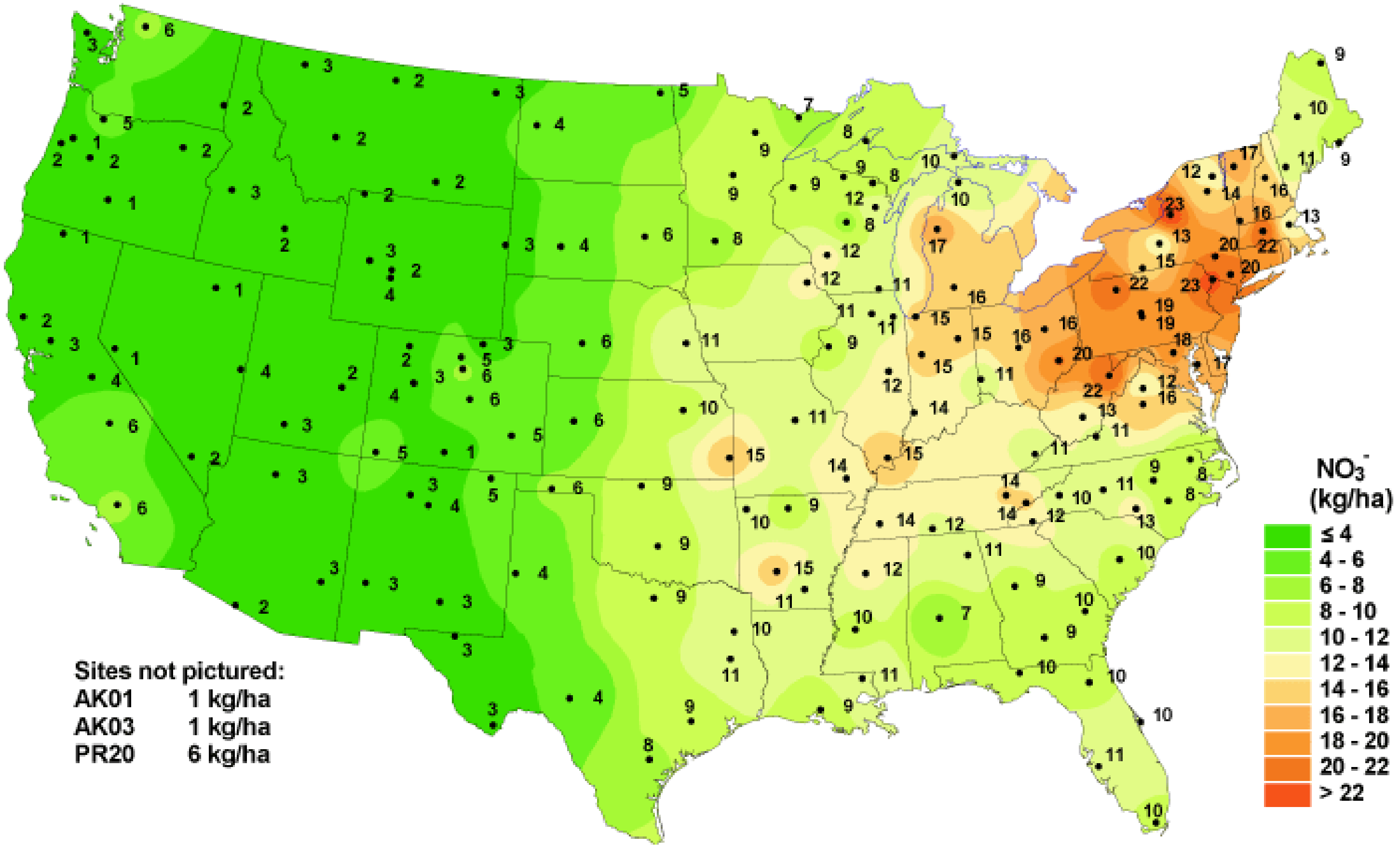
- Nighttime

  $NO_2 + O_3 \rightarrow NO_3 + O_2$

  $NO_3 + NO_2 + M \rightarrow N_2O_5 + M^*$

  $N_2O_5 + H_2O \rightarrow 2HNO_3$

Wet Nitrate Deposition: 1994



$$\frac{?\ \mathrm{g(N)}}{\mathrm{m^2\cdot y}} = \frac{10\ \cancel{\mathrm{kg(NO_3)}}}{\cancel{\mathrm{ha}}\cdot \mathrm{y}}\left(\frac{10^3\ \cancel{\mathrm{g}}}{1\ \cancel{\mathrm{kg}}}\right)\left(\frac{1\ \cancel{\mathrm{ha}}}{10^4\ \mathrm{m^2}}\right)\left(\frac{14.0067\ \mathrm{g(N)}}{62.0049\ \cancel{\mathrm{g(NO_3)}}}\right) = \mathbf{0.23\ g(N)/m^2\cdot y}$$

pH of Acid Rain

- HNO_3 is a “strong” acid: $HNO_3 \rightarrow H^+ + NO_3^-$

  Every mole of HNO_3 produces a mole of H^+
- If 0.23 $g_N/m^2/y$ as HNO_3 are deposited in ≈1 m/y of precipitation, what is the [H+] and pH of the rain?

$$\frac{?\ \text{mol H}^+}{\text{L}} = \frac{0.23\ \cancel{\text{g(N)}}}{\cancel{\text{m}^2}\cdot\cancel{\text{y}}}\left(\frac{1\ \cancel{\text{mol N}}}{14.0067\ \cancel{\text{g(N)}}}\right)\left(\frac{1\ \text{mol H}^+}{1\ \cancel{\text{mol N}}}\right)\left(\frac{1\ \cancel{\text{y}}}{1\ \cancel{\text{m}}}\right)\left(\frac{1\ \cancel{\text{m}^3}}{10^3\ \text{L}}\right)$$

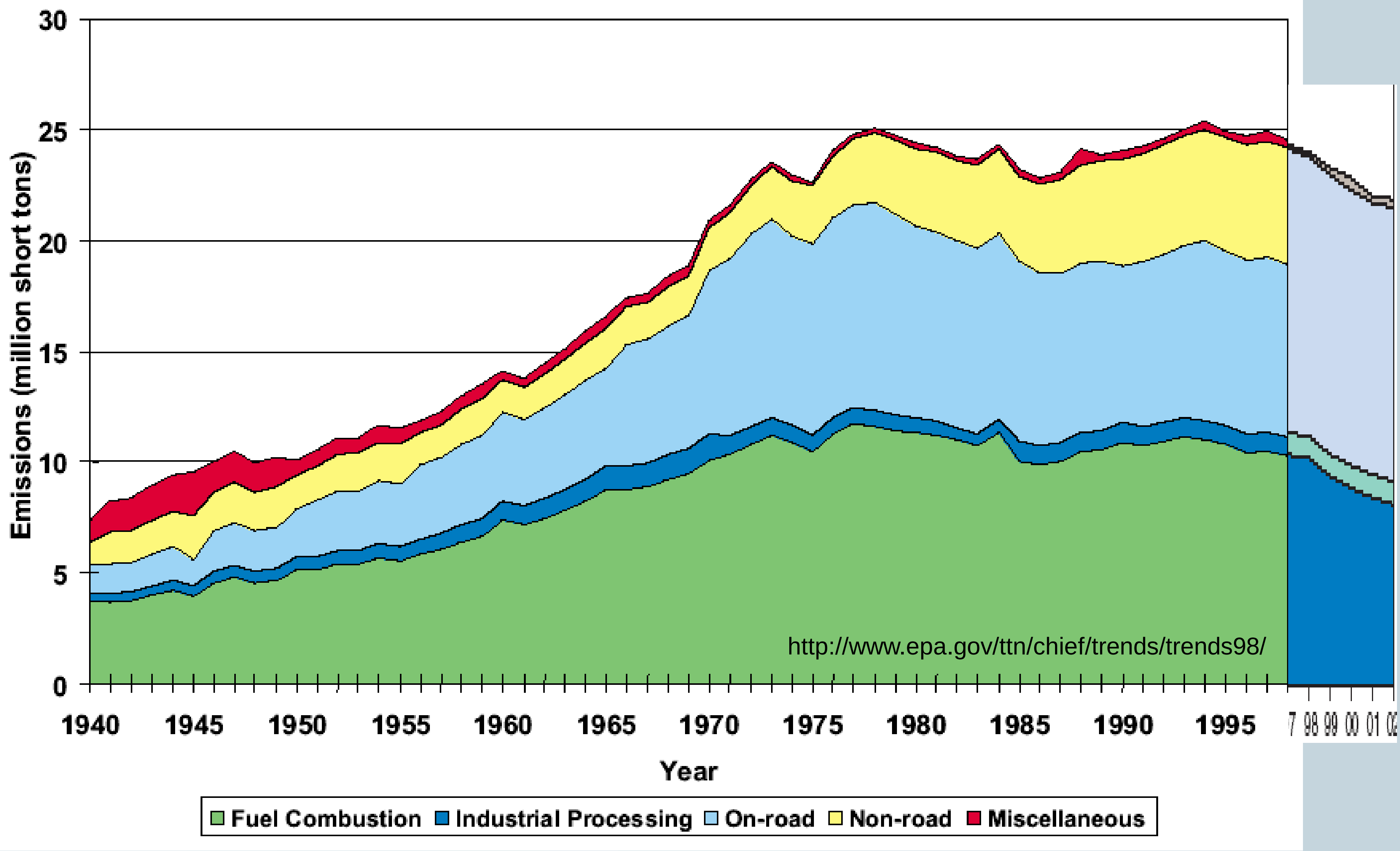
$$= 1.6 \times 10^{-5}\ \text{M H}^+$$

$$\text{pH} = -\log\,[\text{H}^+] = -\log\,(1.6 \times 10^{-5}\ \text{M}) = \mathbf{4.8}$$

- If we also have $[H^+] = 2 \times 10^{-5}$ M from sulfate, then

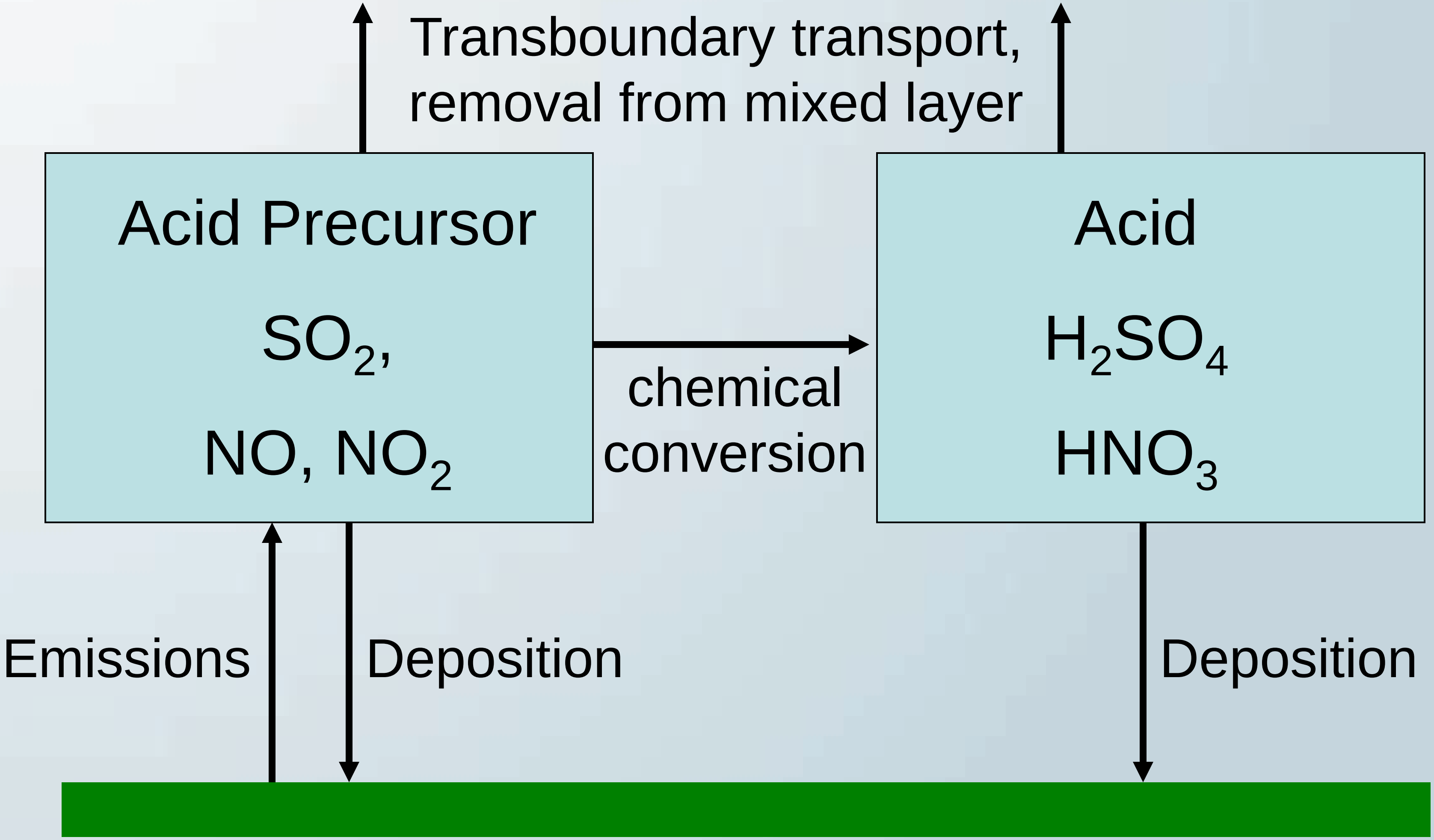
$$\text{pH} = -\log\,(2 \times 10^{-5} + 1.6 \times 10^{-5}) = -\log\,(3.6 \times 10^{-5}) = \mathbf{4.4}$$

US NO_2 Emissions, 1940-2002



http://www.epa.gov/ttn/chief/trends/trends98/

Transport, Conversion, Deposition



Transboundary transport,
removal from mixed layer

Acid Precursor

SO_2,

NO, NO_2

chemical
conversion

Acid

H_2SO_4

HNO_3

Emissions

Deposition

Deposition

Other Natural Effects on pH of Rain

Natural SO_2 Emissions:

$SO_2 + H_2O \leftrightarrow H_2SO_3$

$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$

$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

- bring pH down 0.1 unit (from 5.6 to 5.5)

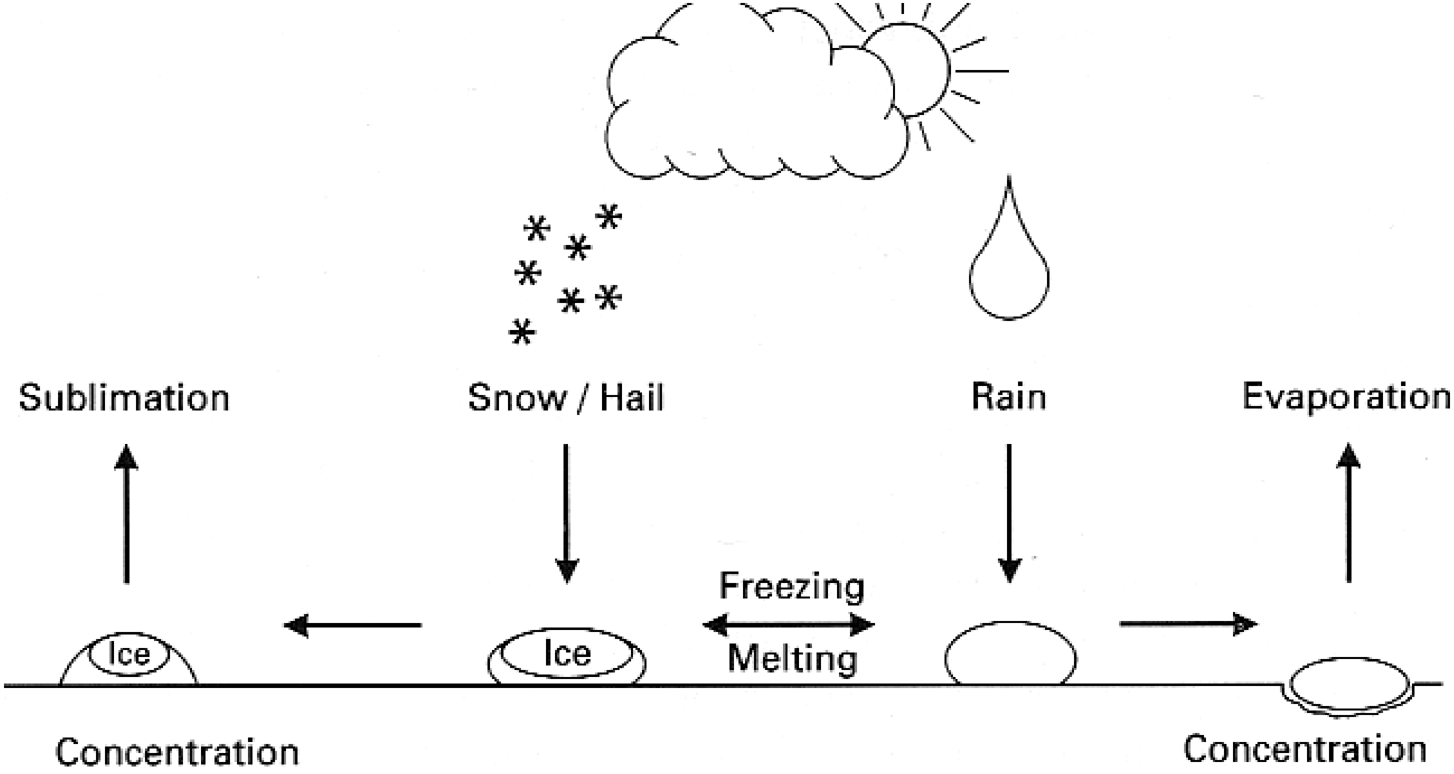
Natural NH_3 Emissions:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

- brings pH up 0.1 unit (from 5.5 to 5.6)

After the Acid Is Deposited

- Evaporation and concentration of wet-deposited acids (on leaf and rock surfaces, in acid snows)



Acid Shock

- Episodic acidification refers to brief periods during which pH levels decrease due to runoff from melting snow.
- Occurs in mid-latitudes where acid snow accumulates in winter, concentrate through evaporation, and melts rapidly in spring.
- Acids are released over a short period of time at concentrations 5 to 10 times more acidic than rainfall.

Acid Neutralization

- Reaction with natural bases

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + CO_2 + H_2O$$

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$

- Nutrient leaching:

$$K\text{-[soil]} + H^+ \rightleftharpoons H\text{-[soil]} + K^+$$

Carbonate Reactions

- Weathering reactions with carbonate minerals (calcite, dolomite, various limestones, etc.):

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

$$CaSiO_3 + 2CO_2 + H_2O \rightleftharpoons Ca^{2+} + SiO_2 + 2HCO_3^-$$

- When acid is added to water, equilibria shift and bicarbonate neutralizes some of the acid:

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2$$

- If soils and sediments are rich in carbonates, weathering will supply additional HCO_3^-.

Alkalinity

- Alkalinity is a measure of the “buffering” or “acid-neutralizing capacity” (ANC) of a solution:

$$\text{ANC} = [\text{HCO}_3^{-}] + 2[\text{CO}_3^{2-}] + [\text{OH}^{-}] - [\text{H}^{+}]$$

- Water saturated with $CaCO_3$:

$$\text{ANC} = 970 \times 10^{-6}\ \text{Eq/L} = 970\ \mu\text{eq/L}$$

  - For bases, an equivalent (Eq) is the amount of a substance which will react with one mole of hydronium ions (H_3O^+).
  - 1 mol CO_3^{2-} = 2 Eq CO_3^{2-}
- ANC depends on watershed soil characteristics.

Buffer Solutions

- A **buffer** is an aqueous solution a weak acid (H_2CO_3) and its conjugate base (HCO_3^-) or a weak base (CO_3^{2-}) and its conjugate acid (HCO_3^-).
    - Conjugate base = acid less one H^+
    - Conjugate base = base plus one H^+

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$[H^+] = K_{a1}\frac{[H_2CO_3]}{[HCO_3^-]}$$

$$[H^+] = K_a\frac{[\text{weak acid}]}{[\text{conjugate base}]}$$

- As long as there are significant concentrations of the weak acid (H_2CO_3) and the conjugate base (HCO_3^-), changing one or the other does not change the ratio of acid to base much so the $[H^+]$ and pH stay relatively constant.

Simplistic Calculation to Illustrate Buffering

- pH pristine natural water is about 5.6.
- Calculate the pH of a solution where enough strong acid is added to water to yield a 0.1 M H^+ solution.

  $$\text{pH} = -\log(10^{-1}) = 1$$

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^-.

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[H^+] = 4.5 \times 10^{-7} \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7} \frac{1\text{ M } H_2CO_3}{1\text{ M } HCO_3^-}$$

$$[H^+] = -\log 4.5 \times 10^{-7} = \mathbf{6.35}$$

Simplistic Calculation to Illustrate Buffering

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^- when enough strong acid is added to the solution to make the solution 0.1 M strong acid.

$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$

$[HCO_3^-] = 1\text{ M} - 0.1\text{ M} = 0.9\text{ M } HCO_3^-$

$[H_2CO_3] = 1\text{ M} + 0.1\text{ M} = 1.1\text{ M } H_2CO_3$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[H^+] = 4.5 \times 10^{-7} \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7} \frac{1.1\text{ M } H_2CO_3}{0.9\text{ M } HCO_3^-}$$

$$[H^+] = \text{-log } 5.5 \times 10^{-7} = \mathbf{6.26}$$

Buffer Solution – Base and Conjugate Acid

- A lake might contain a buffer solution of the base carbonate from the solution of calcium carbonate in limestone and hydrogen carbonate in runoff from weathering of the limestone.

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

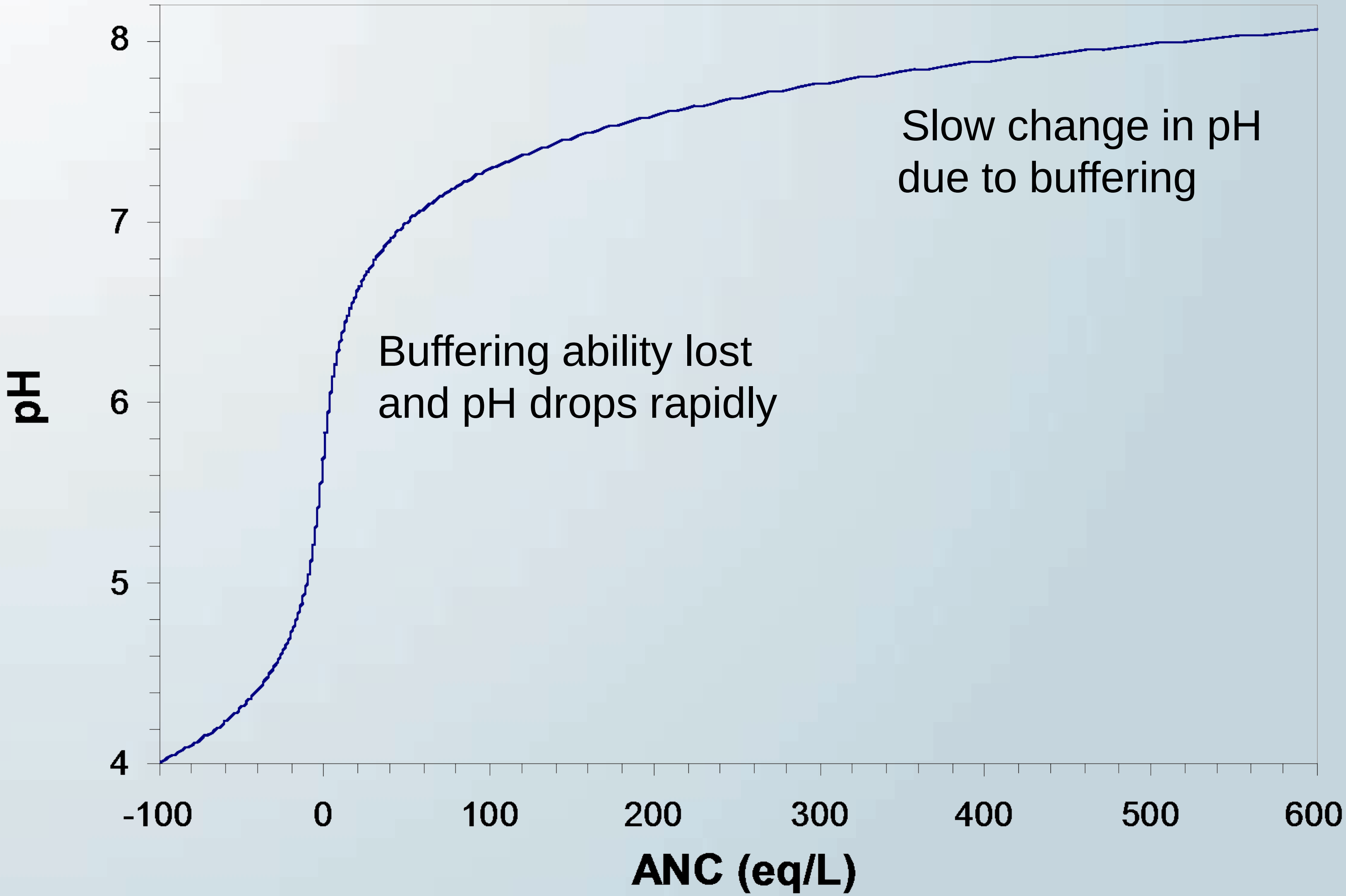
  $CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^{-}$

- Many life forms thrive only in a relatively small pH range so buffer solutions are important for maintaining a near constant pH.

Alkalinity

- Surface water with ANC ≈200 μeq/L is normal; healthy lakes have ANC > 100 μeq/L; water with ANC < 50 μeq/L is highly sensitive to acidification.
- Acidified waters have ANC < 0 μeq/L.
- As acidity [H^+] is added to a lake, ANC is consumed. Because of the buffering, the pH decreases slowly at first, but as the basic components of the buffer react with the acid, the water loses its buffering ability, and the pH drops more rapidly.

pH vs. ANC



Buffering ability lost
and pH drops rapidly

Slow change in pH
due to buffering

Acidification of a Lake

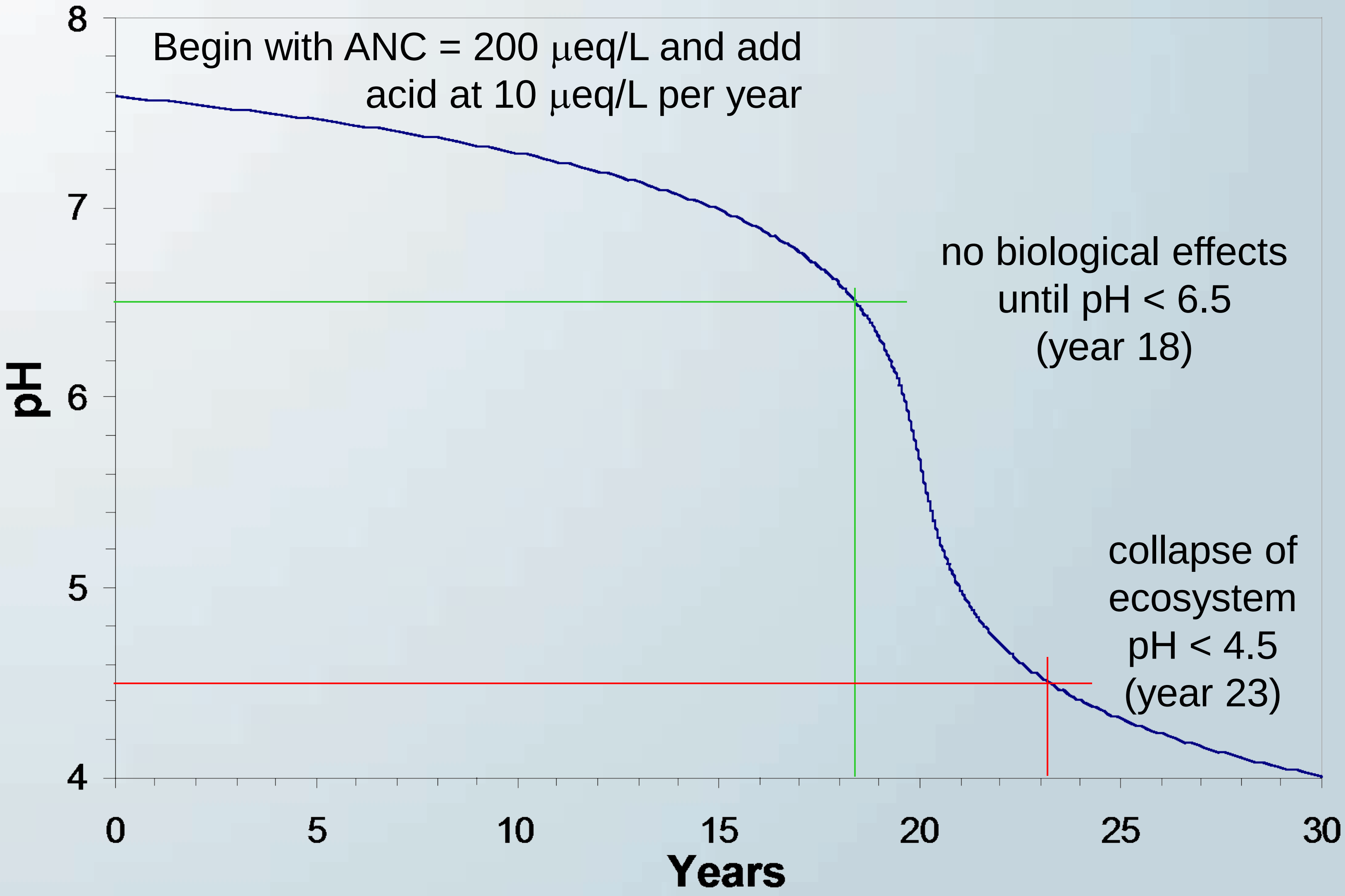
- Assume small lake with a volume of 10^{10} L, a watershed area of 1 km^2, precipitation of 1 m/y with pH = 4 or [H+] = 10^{-4} M. If soils (e.g., granite) do not neutralize the acid, flow of acid in mEq H^+ per liter per year into the lake is:

$$\frac{?\ \mu\text{Eq H}^+}{\text{L}\cdot\text{y}} = \frac{1\ \cancel{\text{km}^2}}{10^{10}\ \text{L}}\left(\frac{10^3\ \cancel{\text{m}}}{1\ \cancel{\text{km}}}\right)^2\left(\frac{1\ \cancel{\text{m}}}{1\ \text{y}}\right)\left(\frac{10^3\ \cancel{\text{L}}}{1\ \cancel{\text{m}^3}}\right)\left(\frac{10^{-4}\ \text{mol H}^+}{1\ \text{L}}\right)\left(\frac{1\ \text{Eq H}^+}{1\ \text{mol H}^+}\right)\left(\frac{10^6\ \mu\text{Eq}}{1\ \text{Eq}}\right)$$

$$\approx 10\ \mu\text{Eq H}^+/\text{L}\cdot\text{y}$$

- ANC would decrease by 10 μeq/L per year.

Acidification of a Lake



Begin with ANC = 200 μeq/L and add acid at 10 μeq/L per year

no biological effects until pH < 6.5 (year 18)

collapse of ecosystem pH < 4.5 (year 23)

Liming the Lake

- After the lake is acidified, we can neutralize the acid by adding lime ($CaCO_3$)

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

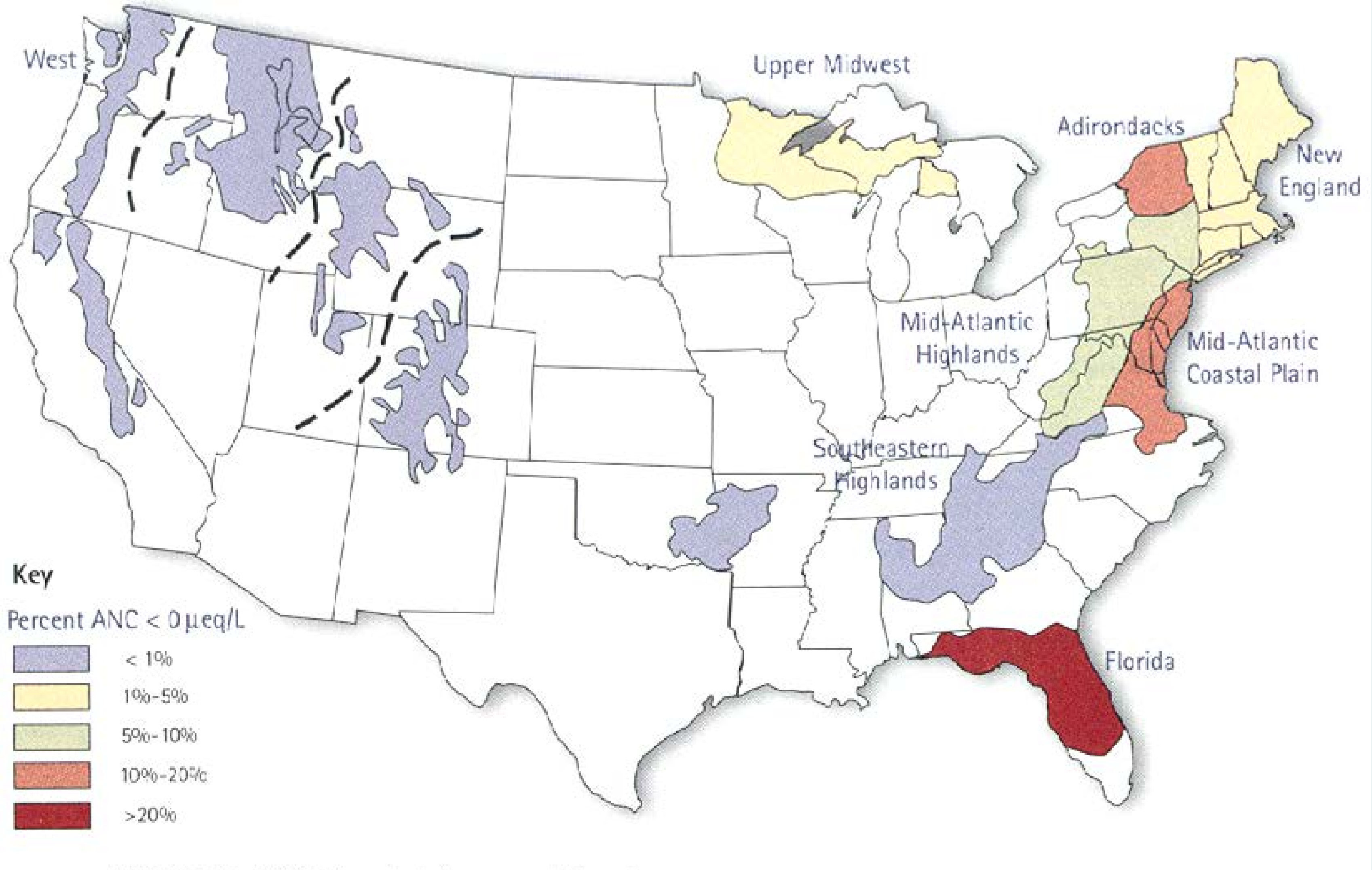
- To raise ANC by 200 μeq/L, we would add:

$$?\ \mathrm{t\ CaCO_3} = 10^{10}\,\cancel{\mathrm{L}}\left(\frac{200\times10^{-6}\ \cancel{\mathrm{Eq}}}{1\ \cancel{\mathrm{L}}}\right)\left(\frac{1\ \cancel{\mathrm{mol\ CaCO_3}}}{2\ \cancel{\mathrm{Eq}}}\right)\left(\frac{100.087\ \cancel{\mathrm{g}}\ \mathrm{CaCO_3}}{1\ \cancel{\mathrm{mol\ CaCO_3}}}\right)\left(\frac{1\ \mathrm{t}}{10^6\ \cancel{\mathrm{g}}}\right)$$

$$= \mathbf{100\ t\ CaCO_3}$$

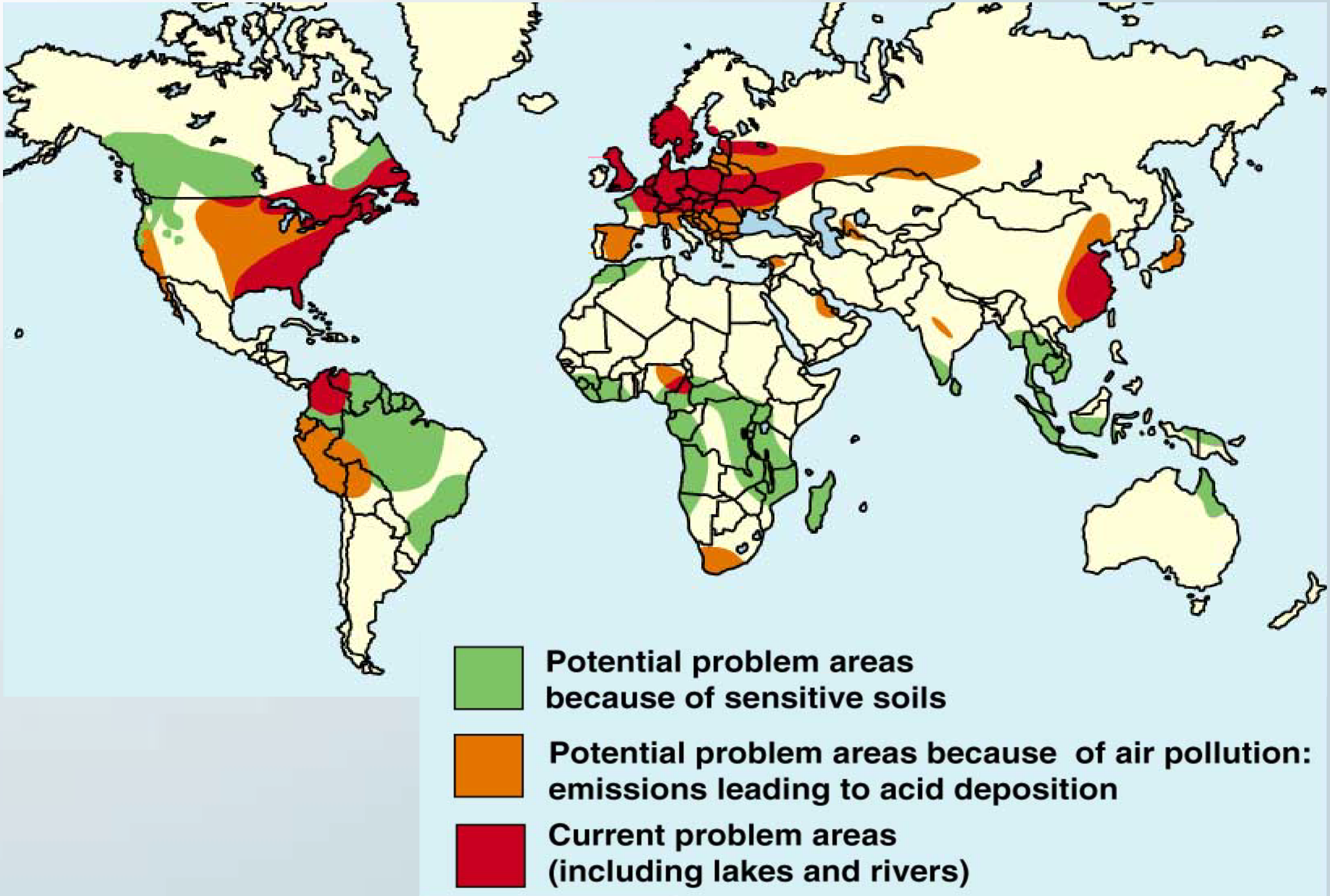
- If the acid flow into the lake continues, this would have to be replenished on a time scale comparable to the residence time of water in the lake (in this case, ≈10 y).

Sensitive Areas



Source: NAPAP. 1991. 1990 Integrated Assessment Report.

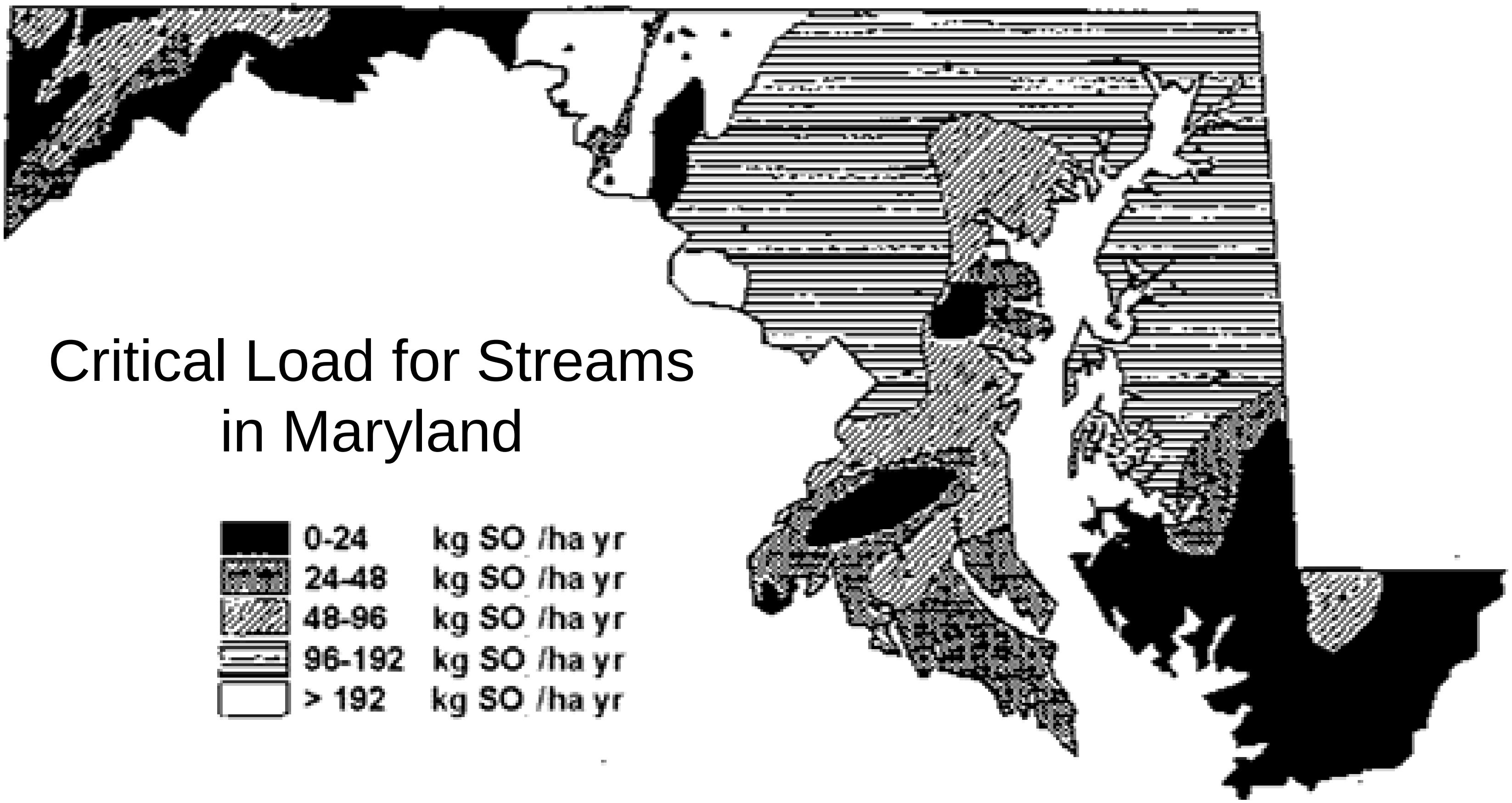
Sensitive Areas



Critical Load

- The maximum amount of acid deposition that a region can receive without damage to its ecosystems is known as its “critical load”.
- CL depends on the ANC of water, rocks, and soils.

Critical Load for Streams in Maryland



$$\frac{?\ \text{mol H}^+}{\text{L}} = \frac{24\ \cancel{\text{kg}}\cancel{(\text{SO}_4)}}{\cancel{\text{ha}}\cdot\cancel{\text{y}}}\left(\frac{10^3\ \cancel{\text{g}}}{1\ \cancel{\text{kg}}}\right)\left(\frac{1\ \cancel{\text{mol}\ (\text{SO}_4)}}{96.0636\ \cancel{\text{g}(\text{SO}_4)}}\right)\left(\frac{2\ \text{mol H}^+}{1\ \cancel{\text{mol}\ (\text{SO}_4)}}\right)\left(\frac{1\ \cancel{\text{y}}}{1\ \cancel{\text{m}}}\right)\left(\frac{1\ \cancel{\text{ha}}}{10^4\ \cancel{\text{m}^2}}\right)\left(\frac{1\ \cancel{\text{m}^3}}{10^3\ \text{L}}\right)$$

$$= 5.0 \times 10^{-5}\ \text{M H}^+$$

$$\text{pH} = -\log\,[\text{H}^+] = -\log\,(5.0 \times 10^{-5}\ \text{M}) = \mathbf{4.3}$$

Nutrient Leaching

- Soil chemistry is governed by negative charge of clay and humus particles, which gives them the ability to retain and exchange cations
- Each ion can displace any ion to its right:

  $H^+ > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > Na^+$

- Because H^+ binds more strongly with the soil particles than nutrients, H^+ displaces nutrients:

  $K\text{-[soil]} + H^+ \leftrightarrow H\text{-[soil]} + K^+$

  K^+ ion is then dissolved in water; unless taken up by plants, it will be leached out

Nutrients in Runoff:
Czechoslovakia, 1976-82

	Concentration in Forest Runoff (kg/ha·yr)		
	Undamaged	Damaged	Ratio
K Potassium	1.9	6.8	3.6
Mg Magnesium	3.8	26	6.8
Ca Calcium	9.9	74	7.5
S Sulfate	9.0	96	10.7
N Nitrate	0.6	12	20
Al Aluminum	0.1	3.2	32

Aluminum Toxicity

- Aluminum hydroxide solid is a base that can react with acid. For example:

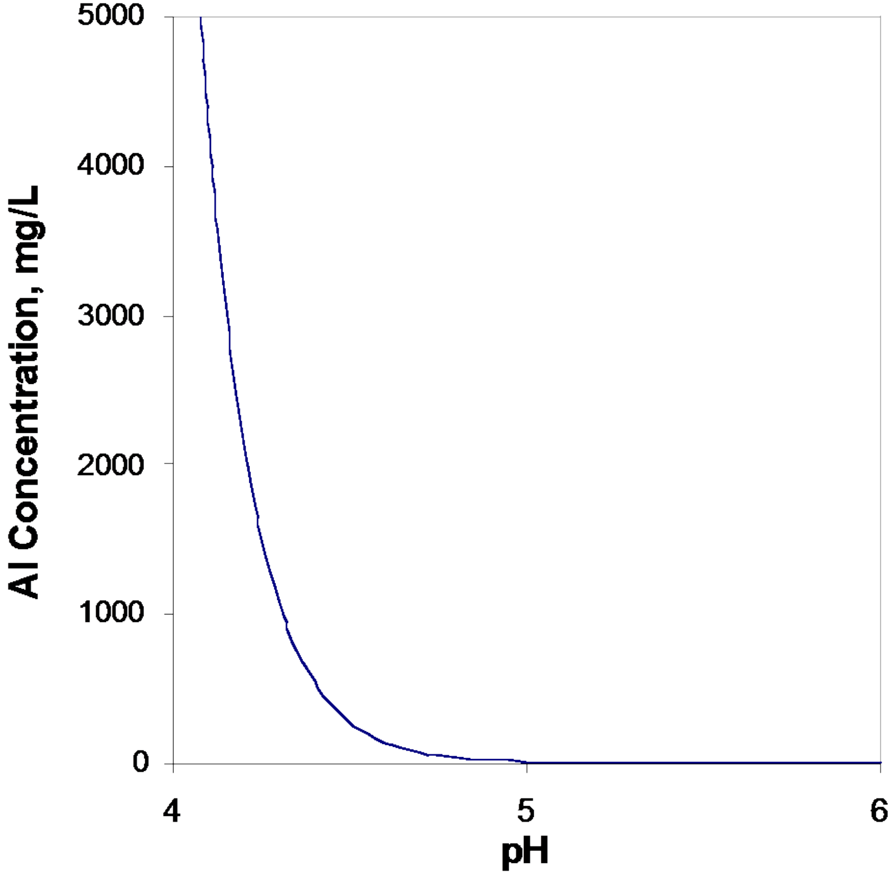
$$\mathrm{Al(OH)_3(s) + 3H^+(aq) \leftrightarrow Al^{3+}(aq) + 3H_2O(l)}$$

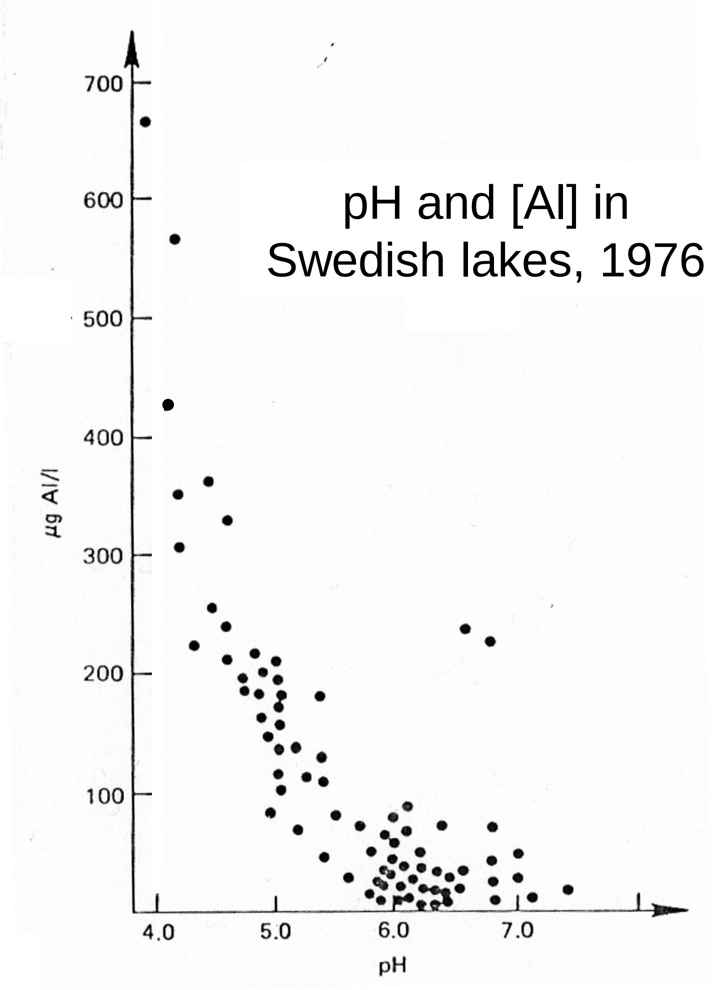
- The Al^{3+} ion is then dissolved in the runoff, which washes into streams and lakes.
- Typical Al concentrations in acidified lakes are 400 to 700 μg/L, increasing with decreasing pH.
- Both low pH and increased aluminum levels are directly toxic to fish.
- In addition, low pH and increased aluminum levels cause chronic stress that may not kill individual fish, but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat.

$Al(OH)_3(s) + 3H^+(aq) \leftrightarrow Al^{3+}(aq) + 3H_2O(l)$

$$\frac{[Al^{3+}]}{[H^+]^3} = 10^{8.5}$$

$$[Al^{3+}] = 10^{8.5}[H^+]^3 = 10^{8.5}\left(10^{-pH}\right)^3 = 10^{8.5-3pH}$$





pH and [Al] in Swedish lakes, 1976

Impacts

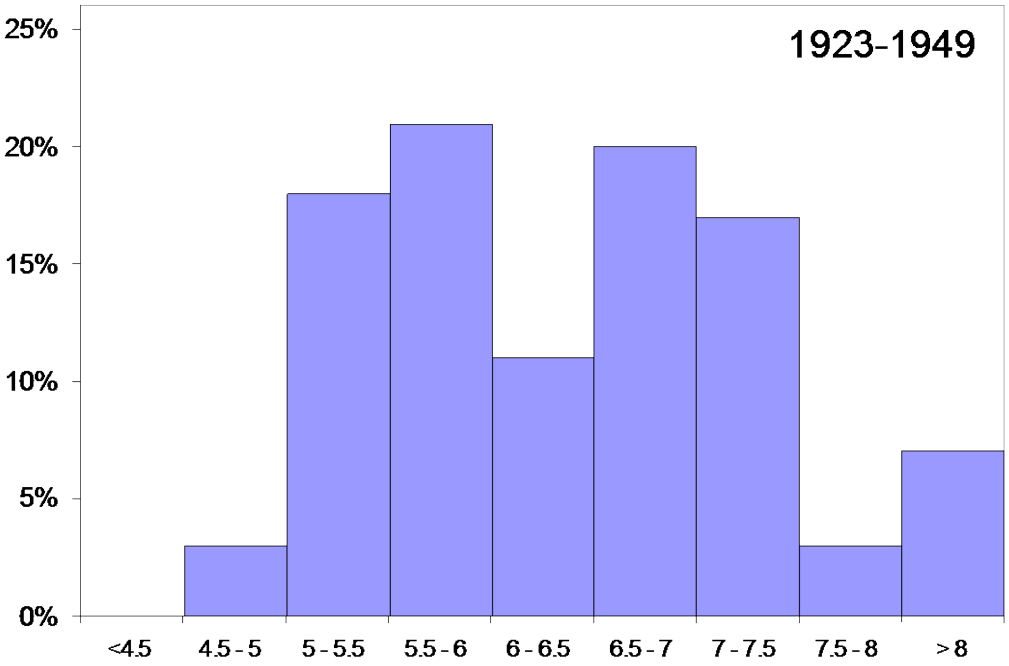
- Freshwater ecosystems
- Forests
- Agriculture
- Human health
- Buildings and property
- Visibility

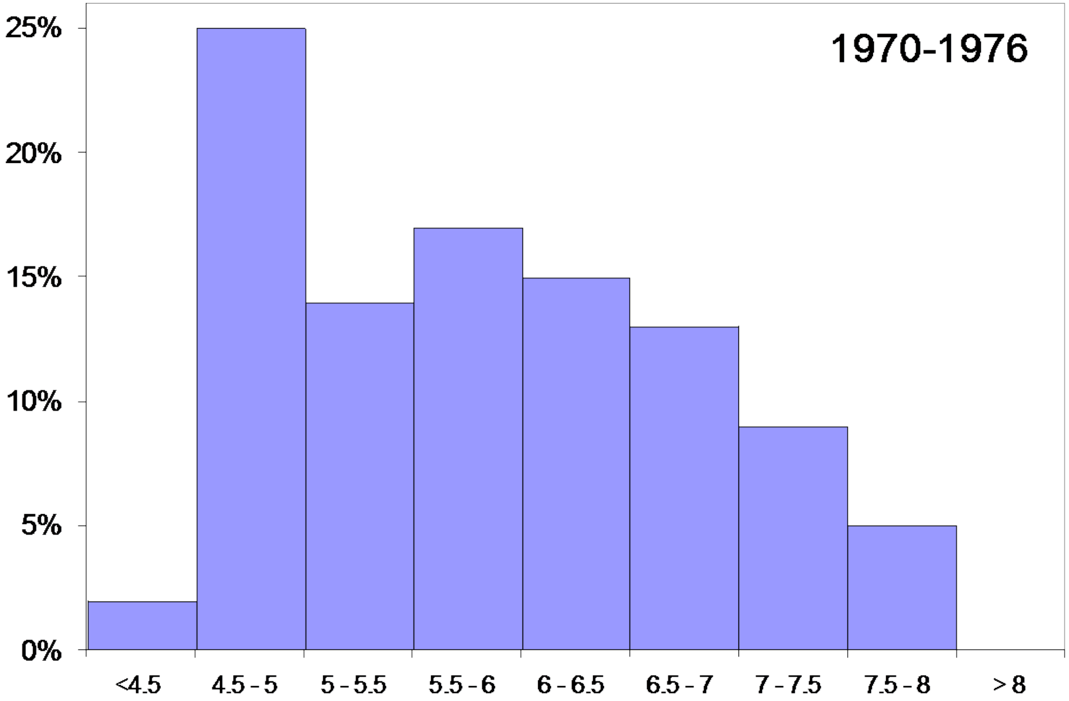
Freshwater Ecosystems

- Areas with combination of high deposition and low ANC are the first effect observed from acid.
- Ecosystem collapsed in ≈15,000 lakes in Scandinavia; serious damage in ≈14,000 in Canada (Ontario), and ≈14,000 in US (Adirondacks)
- Acidity reduces productivity of aquatic plants, microbial activity (decomposition, nutrient cycling)
- At moderate pH (5-6), harm to fish primarily through disruption of food chain and reproductive cycle, not direct damage.
- At low pH, toxic metals (esp. Al) may play a role.

Acidification of lakes in southern Norway

Percent of surveyed lakes with given pH

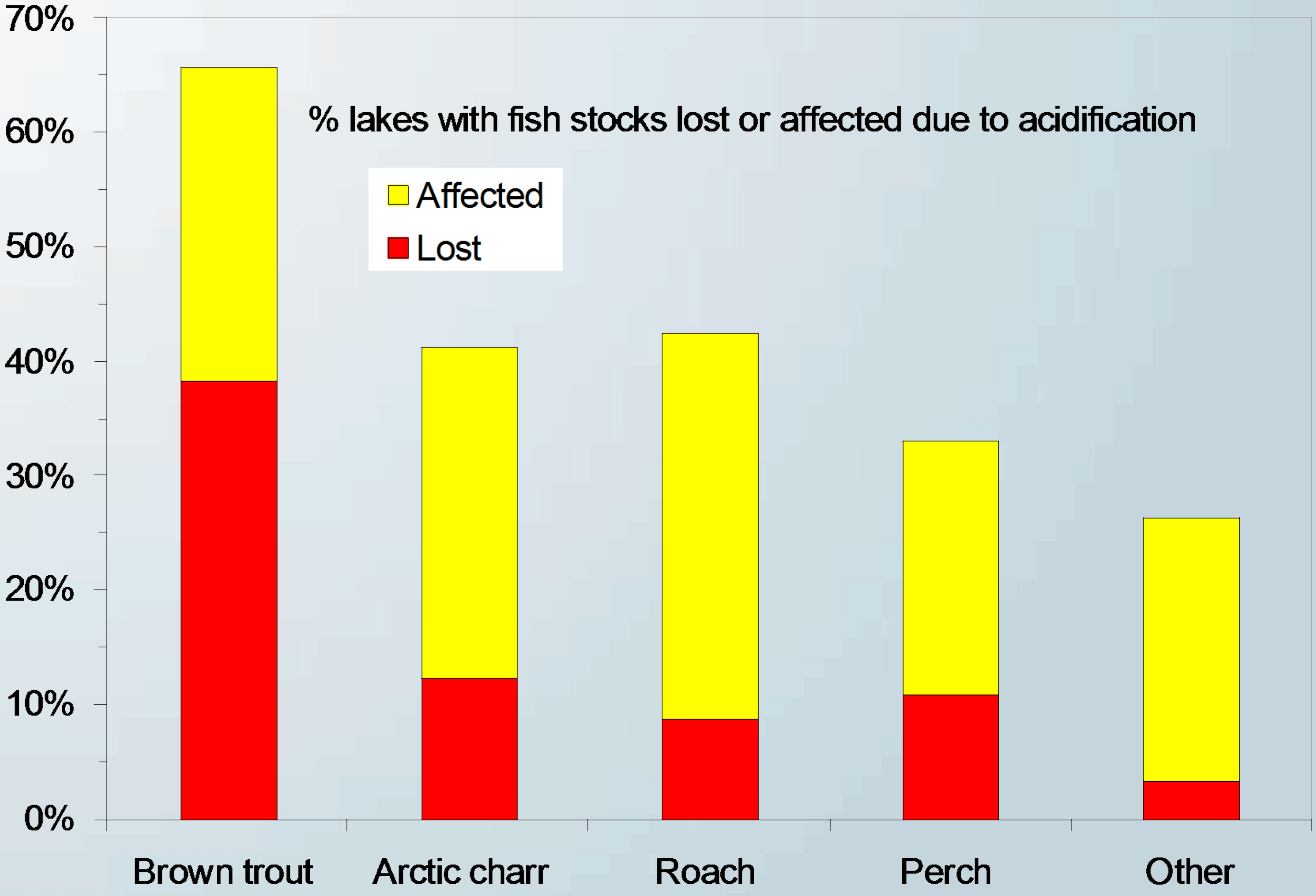




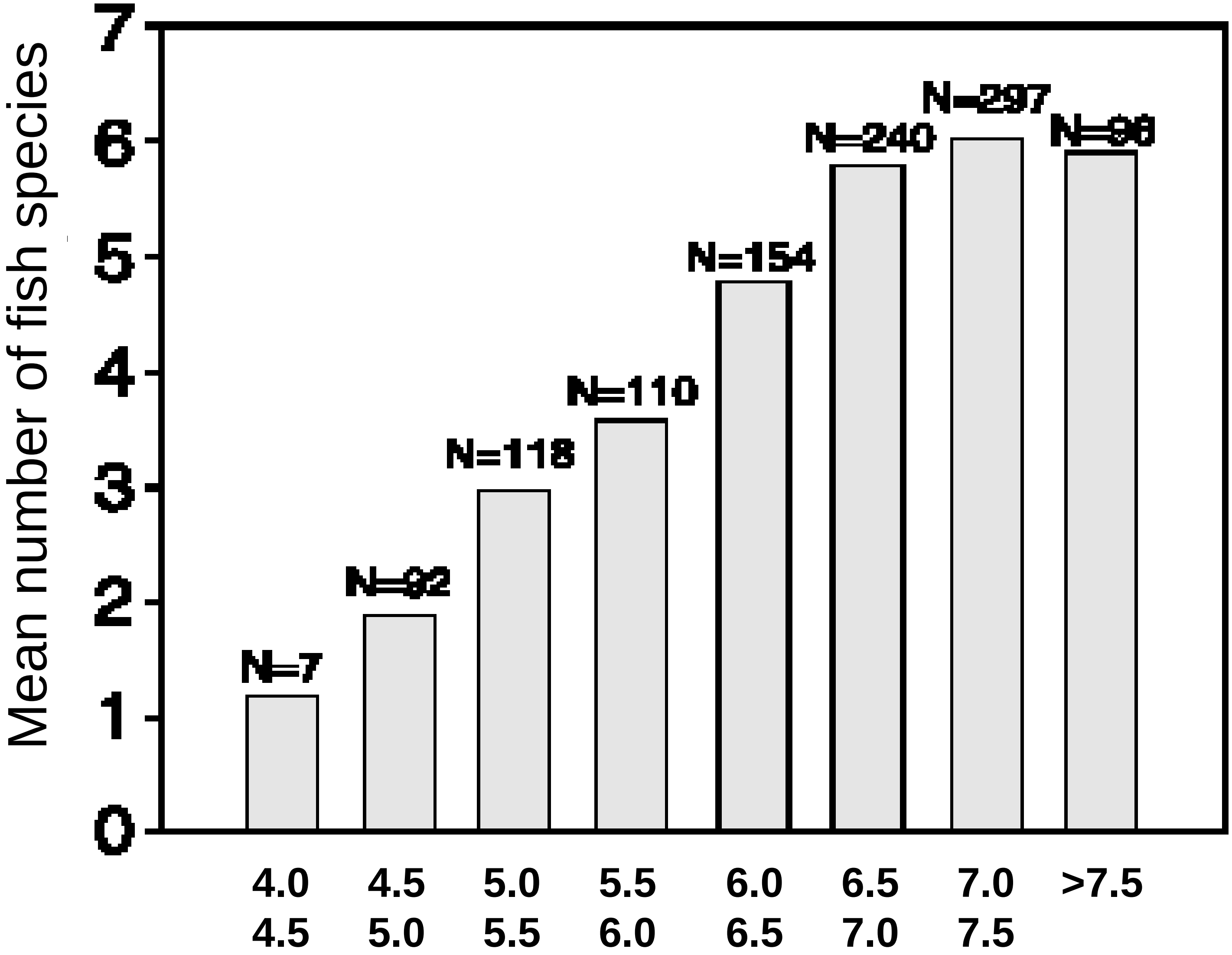
Acid Tolerance of Freshwater Animals

	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	▩	▩	▩			

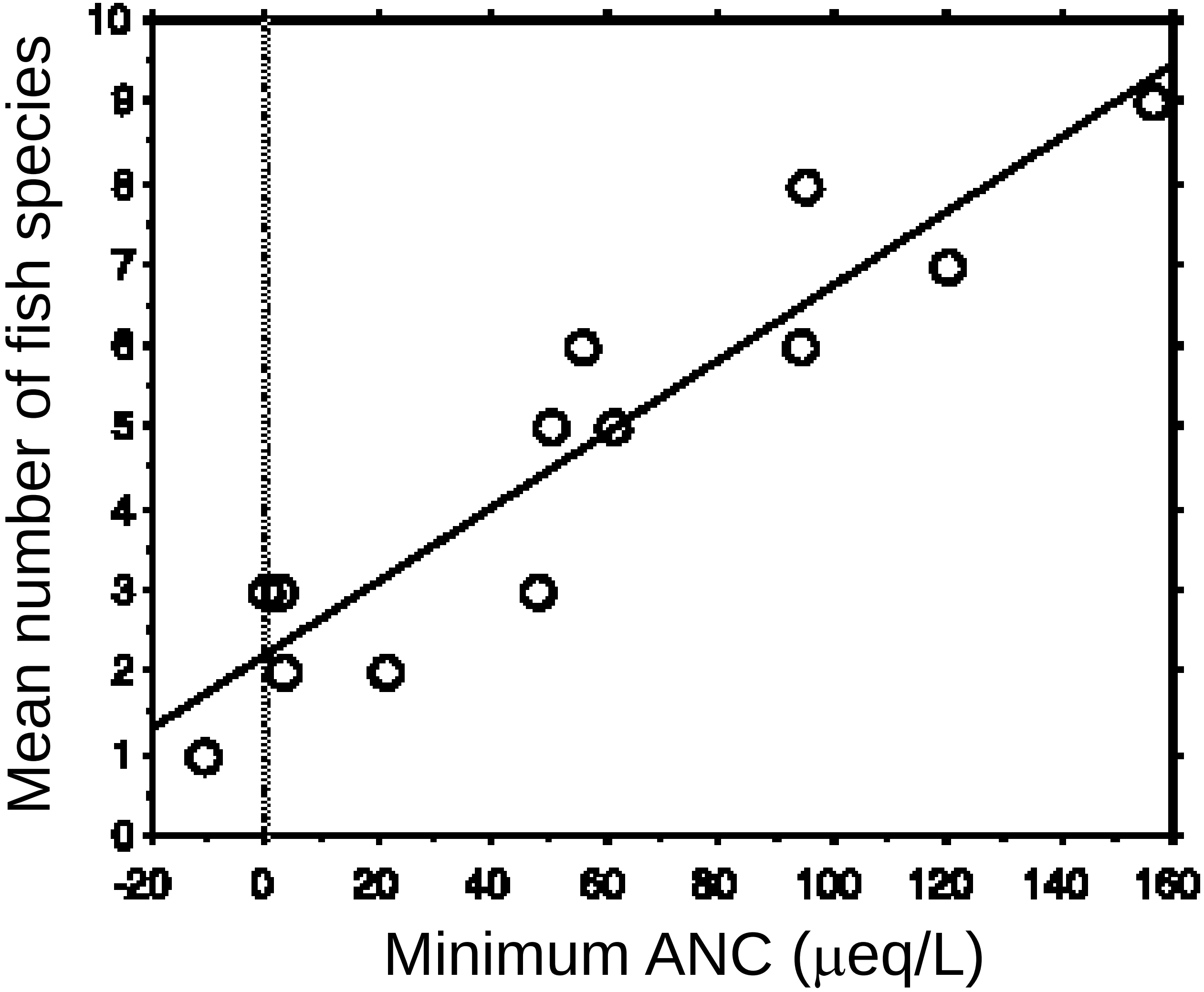
Loss of Fish Stocks in Norway



pH and Number of Species: Adirondacks



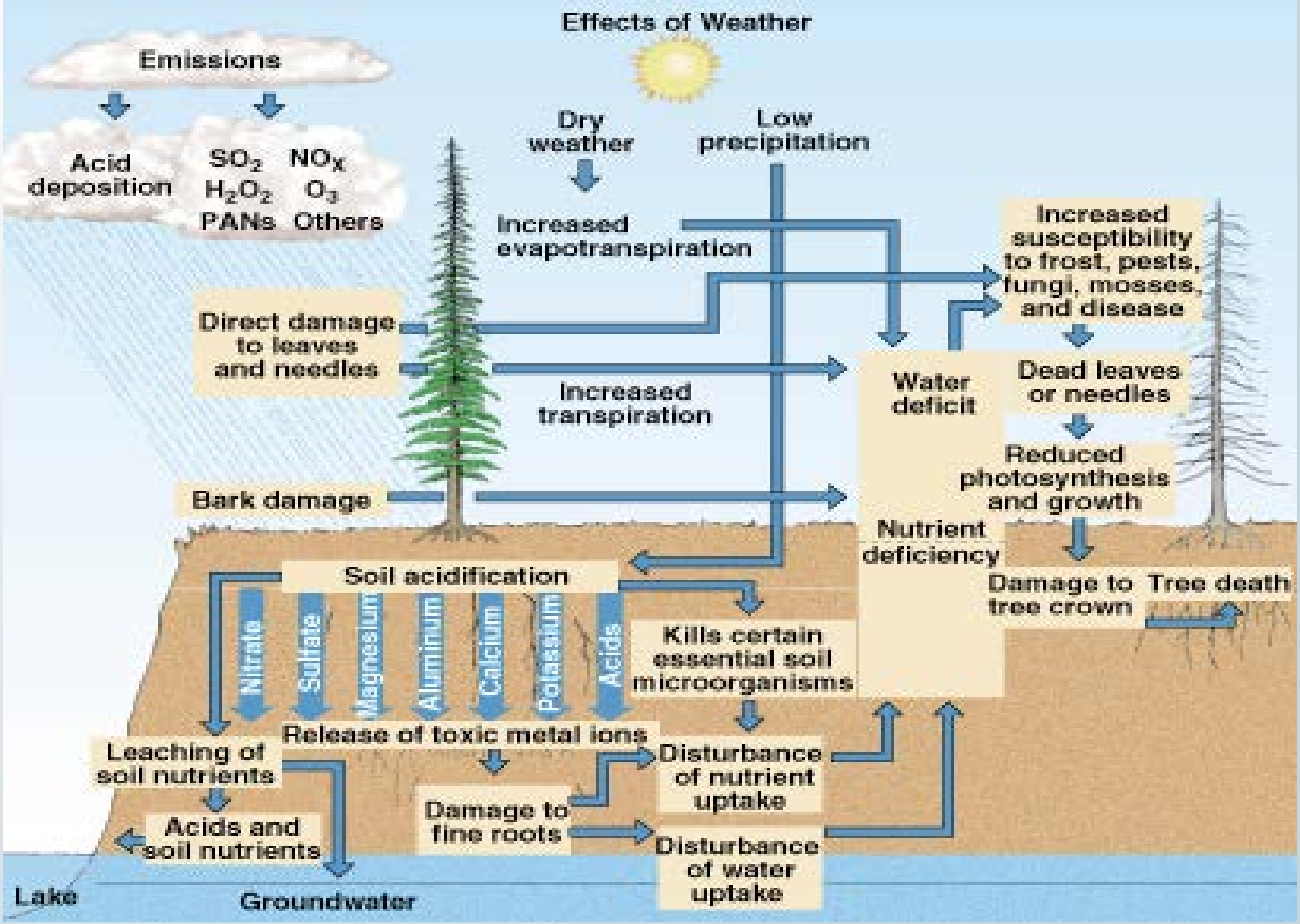
ANC and Fish Species: Adirondacks



Forests and Acid Rain

Forests and Plants

- Forest damage first noticed in Germany in 1970s
  - In Europe, 15% of standing forest damaged
- Acid damage appears to be due primarily to dry deposition and acid fogs
- Also: leach nutrients, suppress microbes (nutrient cycling), mobilize toxic metals (inhibit water, nutrient uptake by fine roots)
- In U.S., Scandinavia, no clear correlation between wet deposition and damage
- Other explanations: disease, pests, ozone, UVB, climate change (more vulnerable due to acid?)


Effects of Weather
Emissions
Acid deposition
SO_2 NO_x
H_2O_2 O_3
PANs Others
Dry weather
Low precipitation
Increased evapotranspiration
Increased susceptibility to frost, pests, fungi, mosses, and disease
Direct damage to leaves and needles
Increased transpiration
Water deficit
Dead leaves or needles
Reduced photosynthesis and growth
Bark damage
Nutrient deficiency
Soil acidification
Damage to tree crown
Tree death
Nitrate
Sulfate
Magnesium
Aluminum
Calcium
Potassium
Acids
Kills certain essential soil microorganisms
Release of toxic metal ions
Leaching of soil nutrients
Disturbance of nutrient uptake
Damage to fine roots
Acids and soil nutrients
Disturbance of water uptake
Lake
Groundwater

Human Health

- Acids
  - Consumption of fish with elevated concentrations of toxic metals (Al, Pb, Cd, Hg, Cu, Zn)
  - Corrosion of pipes resulting in excess levels of Cu, Zn, Pb
    - In Adirondacks, Pb levels up to 100 × standard
- Acid precursors
  - SO_2 and NO_x are toxic;
  - NO_x react to form ozone
  - Respiratory and cardiac diseases

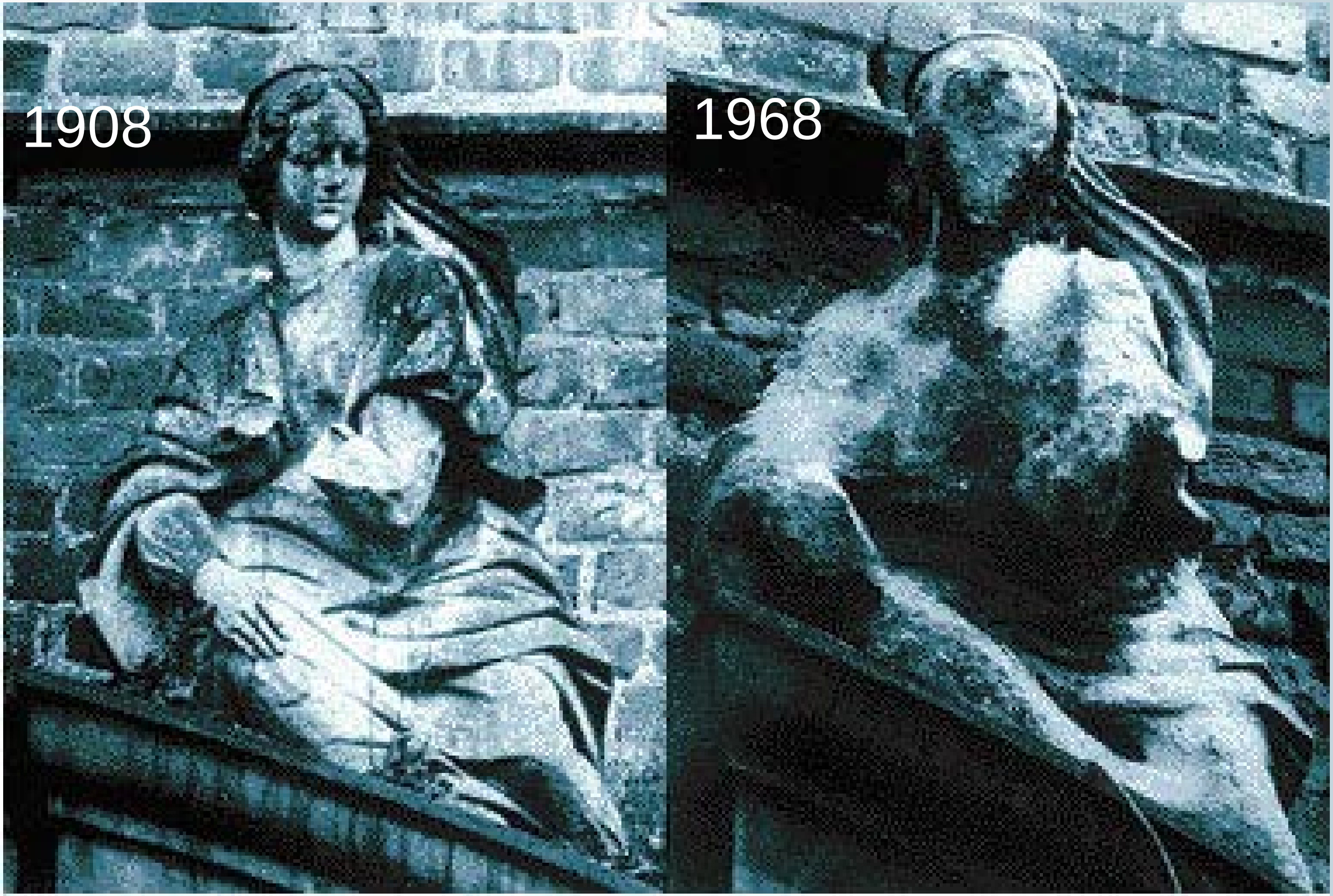
Buildings and Property

- Carbonate stones (marble, limestone, etc.), cement, mortar are dissolved by acids:

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

- Acids etch glass; damage roofing and other building materials; damage plastics and paint (esp. automotive paint)
- Damage to U.S. buildings: ≈$5 billion/y

Capitol Building, Ottawa



Jefferson Memorial

Marble surfaces develop a rough "sugary" texture because calcite grains are loosened as the edges dissolve

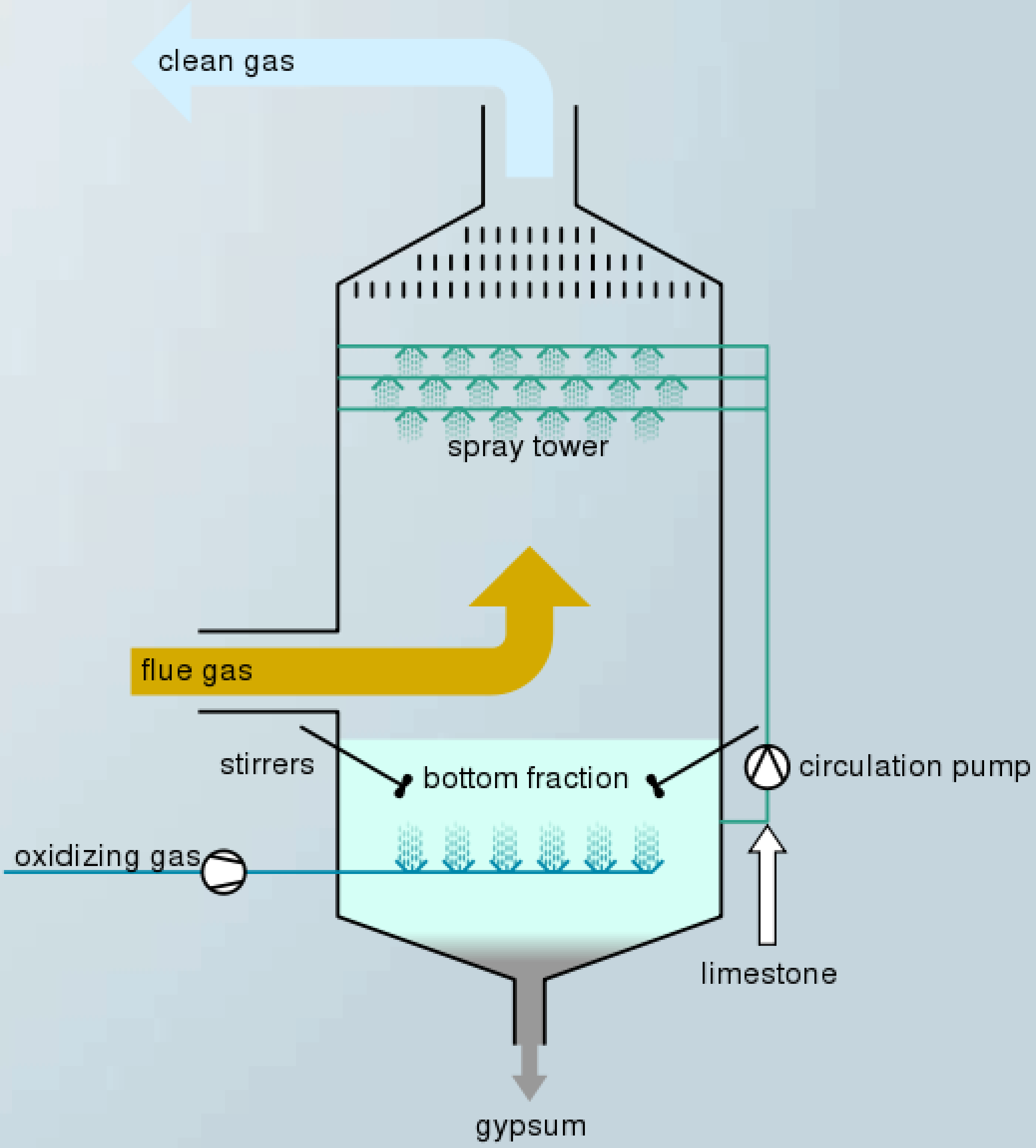
Effects on Metals

Mitigation

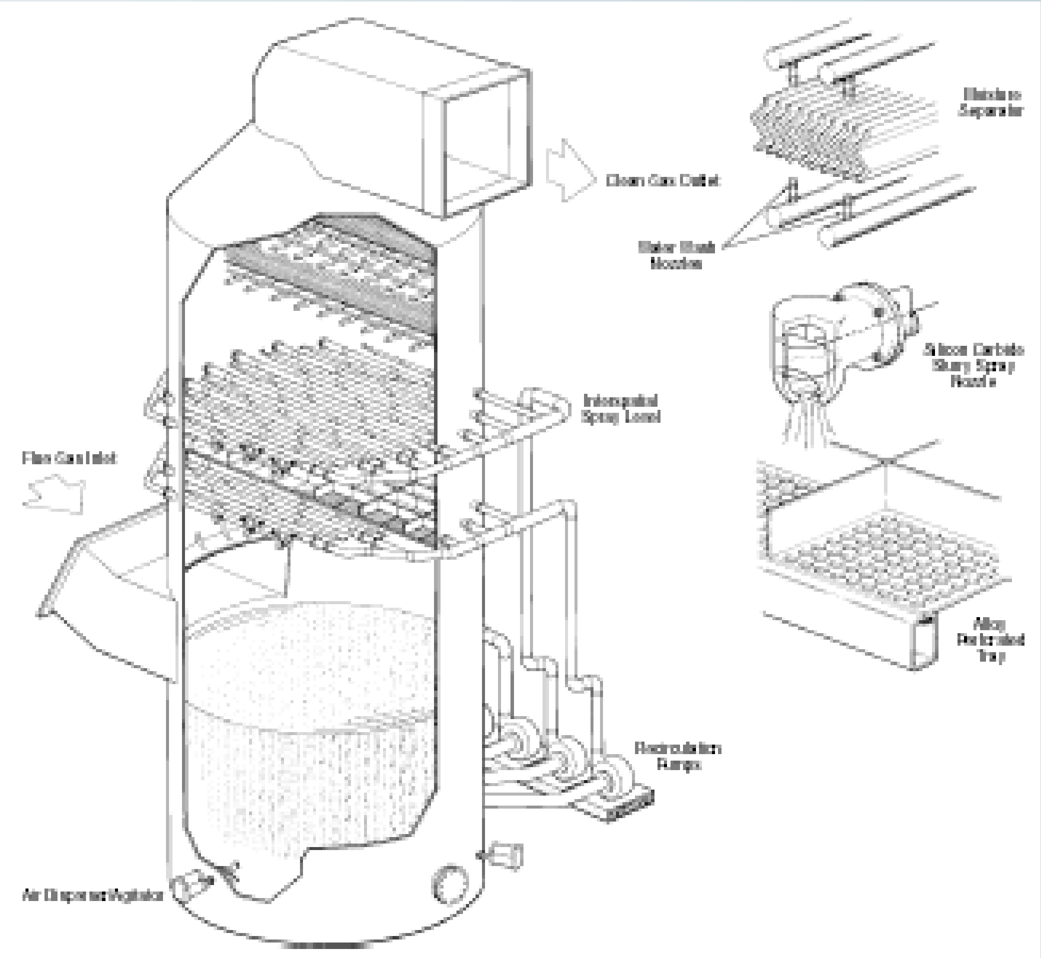
- Tall Stacks (export pollution)
- Sulfur
  - Switch from coal to natural gas (0.001% S)
  - Switch to low-sulfur coal
    - S content ranges from 0.3 to 6%; only 8% of US coal would meet 1975 NSPS (<0.7% S)
  - Scrub coal (solvent refining removes up to 75% S)
  - Flue-gas desulfurization (FGD)
    - mix exhaust gas with lime (CaO); SO_2 reacts for form gypsum ($CaSO_4$)

SO_2 Emissions Reduction

- Due largely to the US EPA's Acid Rain Program, the U.S. had a 33% decrease in SO_2 emissions between 1983 and 2002.
- Partly from flue-gas desulfurization.



Wet SO_2 Scrubber



Flue-Gas Desulfurization

- A technology that enables SO_2 to be removed in power plants burning sulfur-containing coal or oil.
- Wet scrubbing uses a $CaCO_3$ (limestone) slurry and produces $CaSO_3$ (calcium sulfite):

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$$

- When wet scrubbing with a $Ca(OH)_2$ (lime) slurry, the reaction also produces $CaSO_3$ is:

$$Ca(OH)_2(s) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$$

- When wet scrubbing with a $Mg(OH)_2$, the reaction produces $MgSO_3$:

$$Mg(OH)_2(s) + SO_2(g) \rightarrow MgSO_3(s) + H_2O\ (l)$$

- To partially offset the cost of the FGD installation, in some designs, the $CaSO_3$ is further oxidized to produce marketable $CaSO_4 \cdot 2H_2O$ (gypsum).

$$CaSO_3(s) + \tfrac{1}{2}O_2(g) \rightarrow CaSO_4(s)$$

Mitigation – Coal Gasification

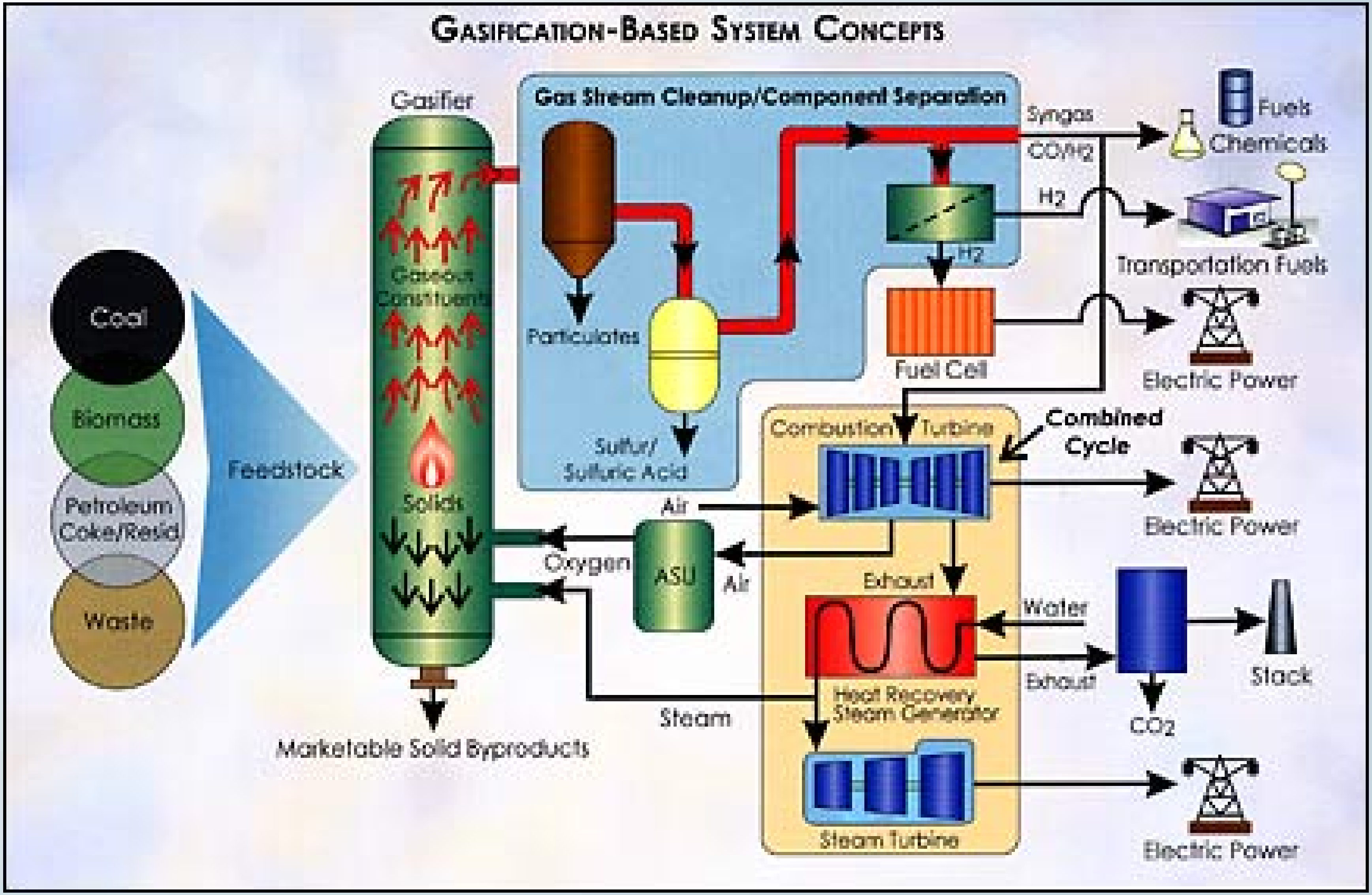
- A gasifier converts hydrocarbon feedstock into gaseous components by applying heat under pressure in the presence of steam.
- Only a relatively small portion of the fuel burns completely. This "partial oxidation" process provides the heat.
- Produce "syngas”, primarily hydrogen and carbon monoxide

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

- Sulfur converted to hydrogen sulfide, H_2S, and carbonyl sulfide, OCS, which can be converted into elemental sulfur or sulfuric acid, both valuable byproducts.
- 99+% of S removed

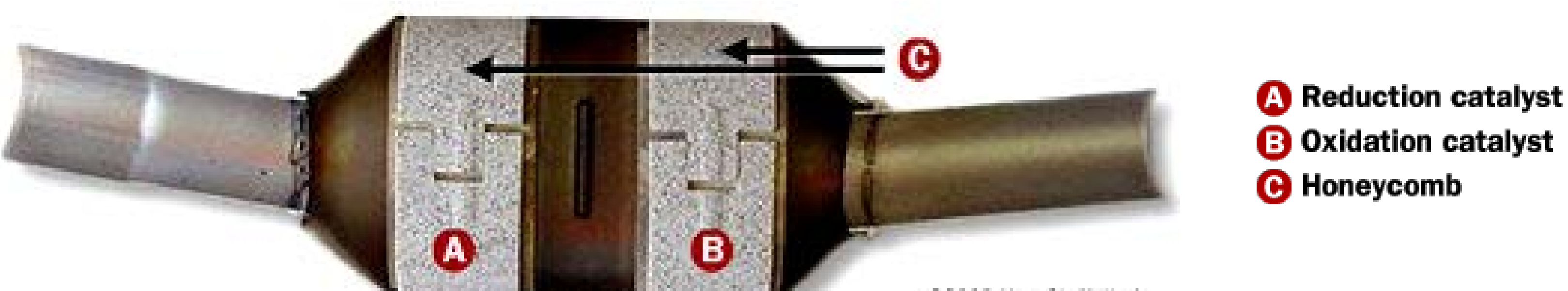
Coal Gasification



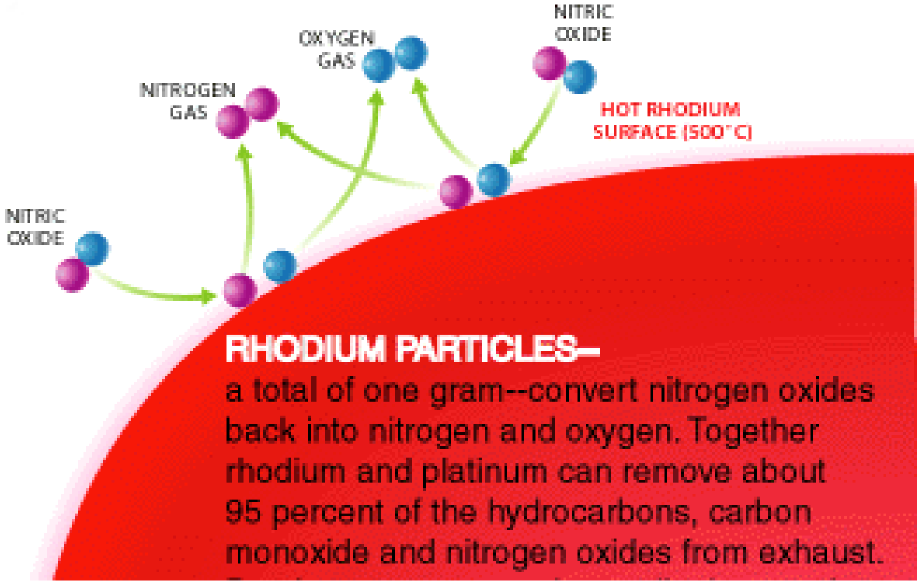
Automobile Catalytic Converters

Catalytic converters: up to 95% reduction in NO_x

$2NO \rightarrow N_2 + O_2$ $2NO_2 \rightarrow N_2 + 2O_2$



©2000 How Stuff Works



RHODIUM PARTICLES— a total of one gram--convert nitrogen oxides back into nitrogen and oxygen. Together rhodium and platinum can remove about 95 percent of the hydrocarbons, carbon monoxide and nitrogen oxides from exhaust.

Standards

- National Ambient Air Quality Standards (NAAQS) – part of Clean Air Act (CAA)

  http://www.epa.gov/air/criteria.html

  http://www.epa.gov/air/caa/
- Two way to achieve standards:
  - Command-and-control
    - Emission and technology standards
  - Market-based mechanisms
    - Taxes and tradable permits
    - Cap-and-trade with free permits: guaranteed reduction, property rights to existing polluters

Clean Air Act Amendments of 1990

Title I: NAAQS and schedule for attainment

Title II: Emission standards for mobile sources

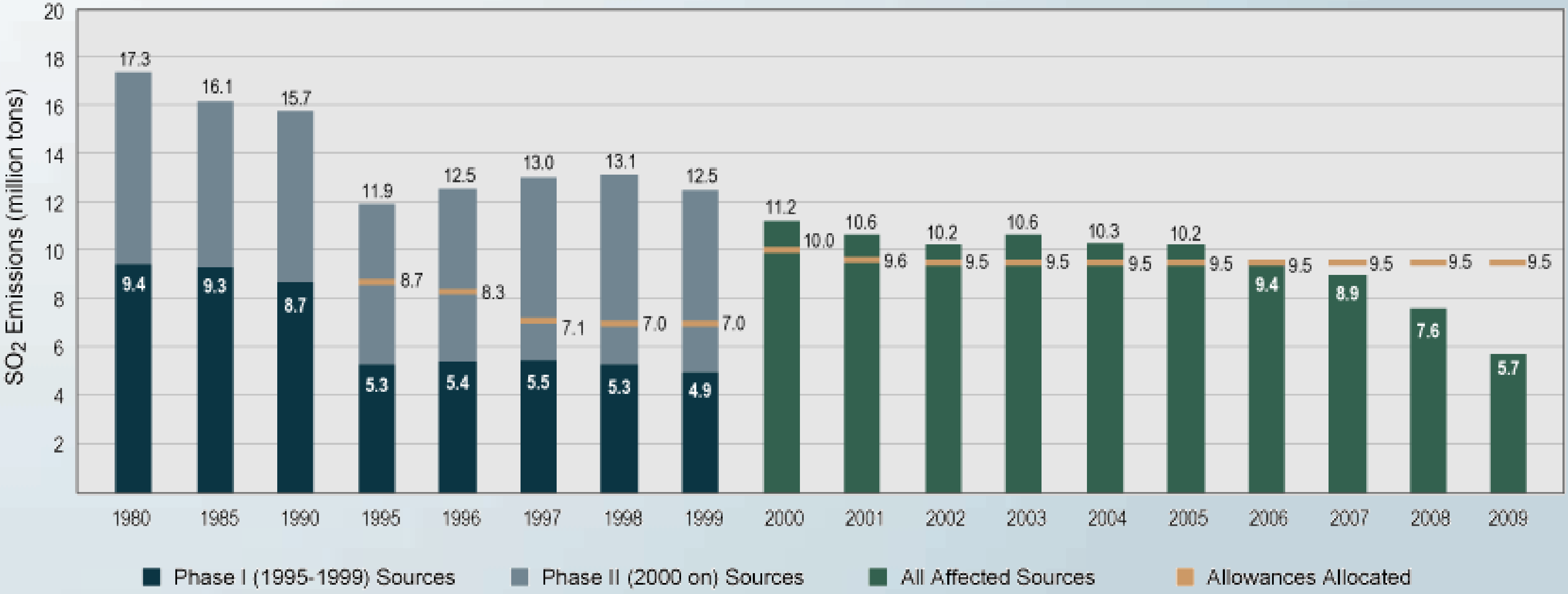
Title IV: Acid Deposition Control

- 10 Mt(SO_2) reduction below 1980 level by 2007; coal-fired utilities from 17.5 → 8.5 Mt
  - Phase I: 110 high-emitting plants (10.9 → 8.7 Mt)
  - Phase II: all plants > 25 MW, 8.5 Mt cap
- 2 Mt(NO_x) reduction in 2 phases, based on emission rates, achieved w/low-NO_x burners
  - cost = $230/t v. $7000/t for cars

Tradable Permit System for SO_2

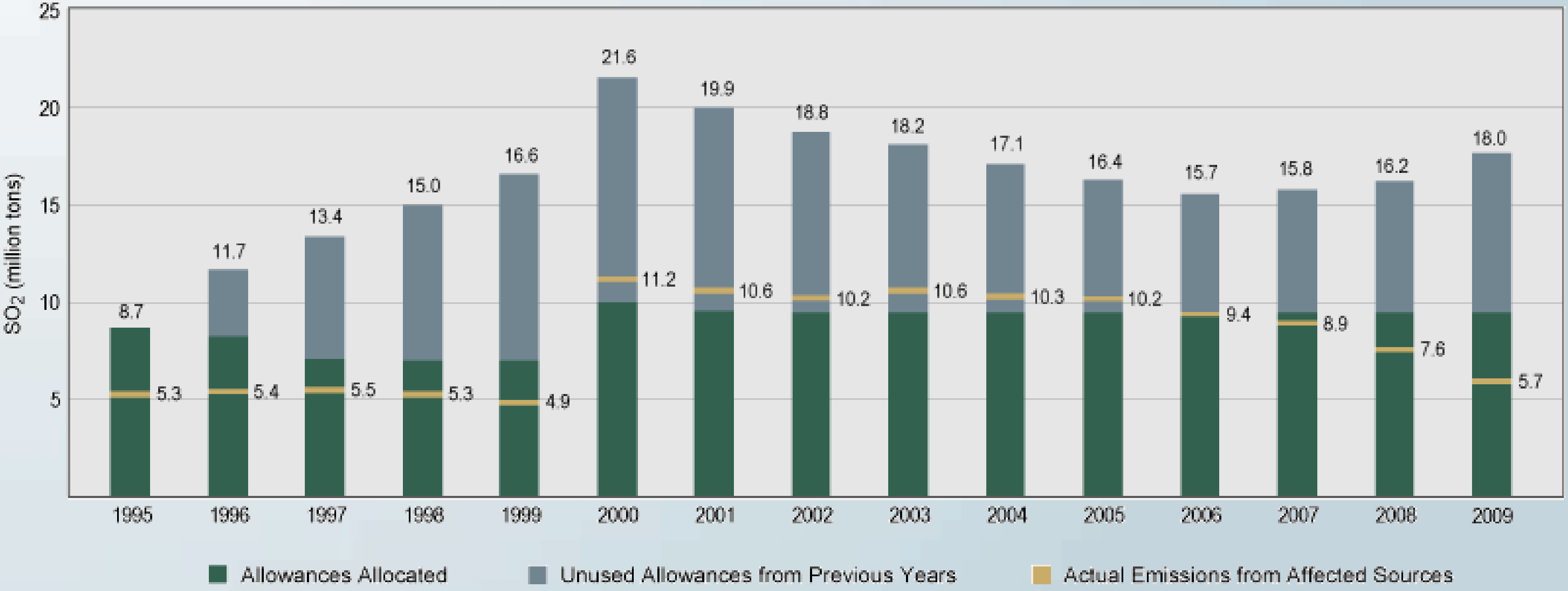
- Beginning in 1995, emissions $\leq$ allowances
- Allocation:
  - existing plants: 2.5 lb/MBTU (Phase I), 1.2 lb/MTU (Phase II), based on 1985-87 average emissions
  - new plants must purchase permits
  - 2.8% withheld for auction by EPA
  - direct sale @ $1500/t
- Unused allowances can be traded, banked
- Voluntary opt-in for other sources
- Continuous emission monitoring; allowance tracking
- Penalty = $2000/t plus allowances
- Ignores location of sources

SO_2 Emissions from Acid Rain Program Sources, 1980–2009



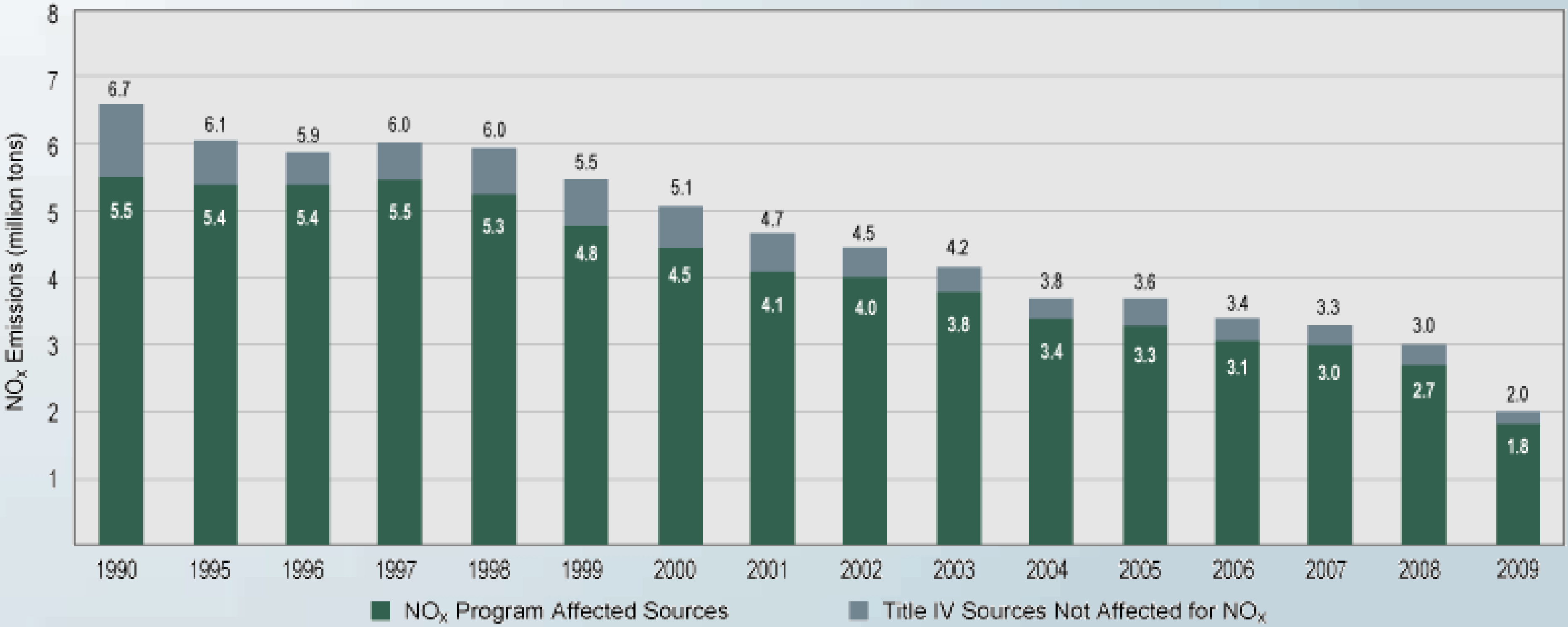
http://www.epa.gov/airmarkets/progress/ARP09_1.html

SO_2 Emissions and the Allowance Bank, 1995–2009



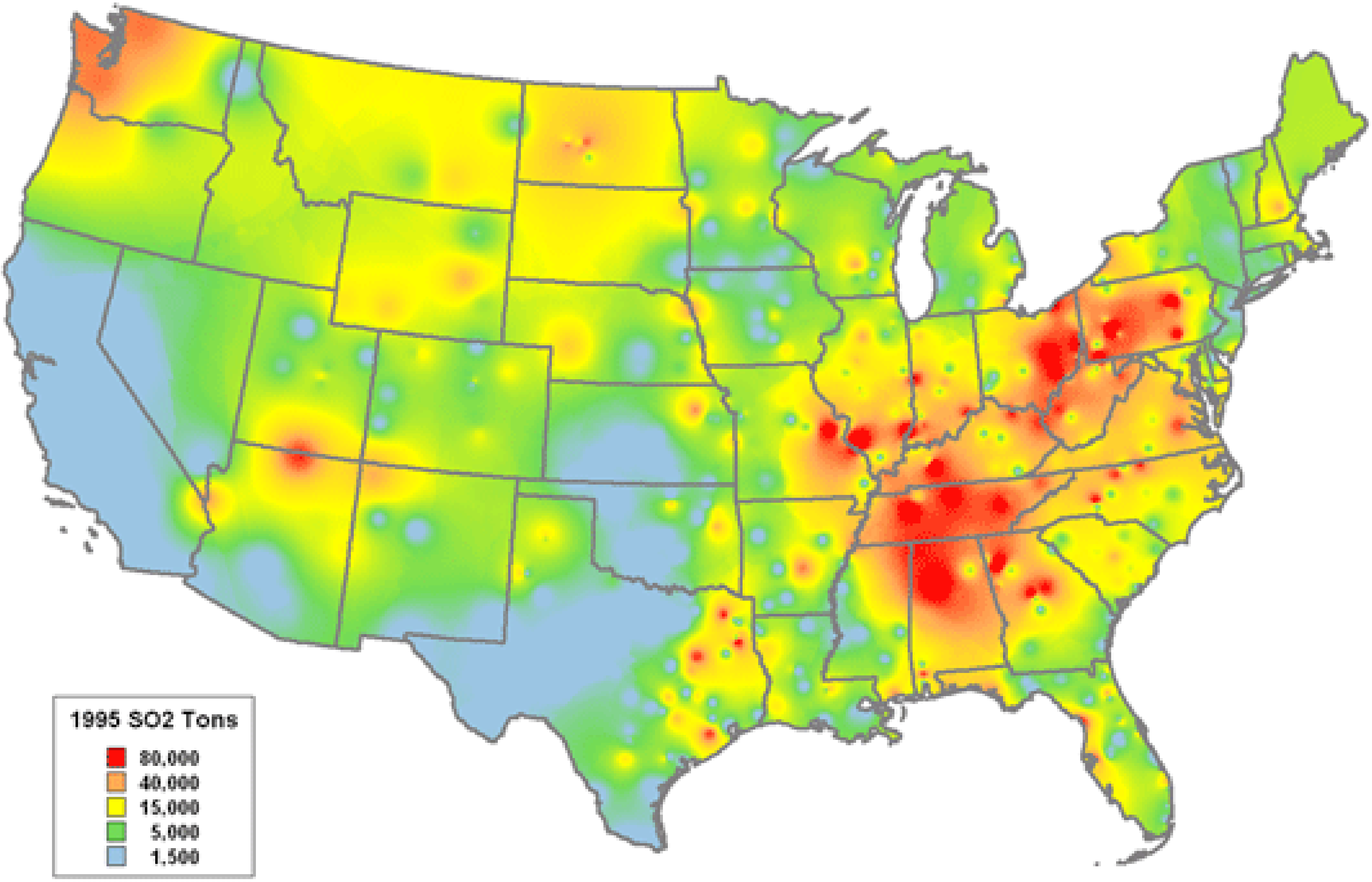
http://www.epa.gov/airmarkets/progress/ARP09_1.html

NO$_x$ Emission Trends for All Acid Rain Program Units, 1990–2009

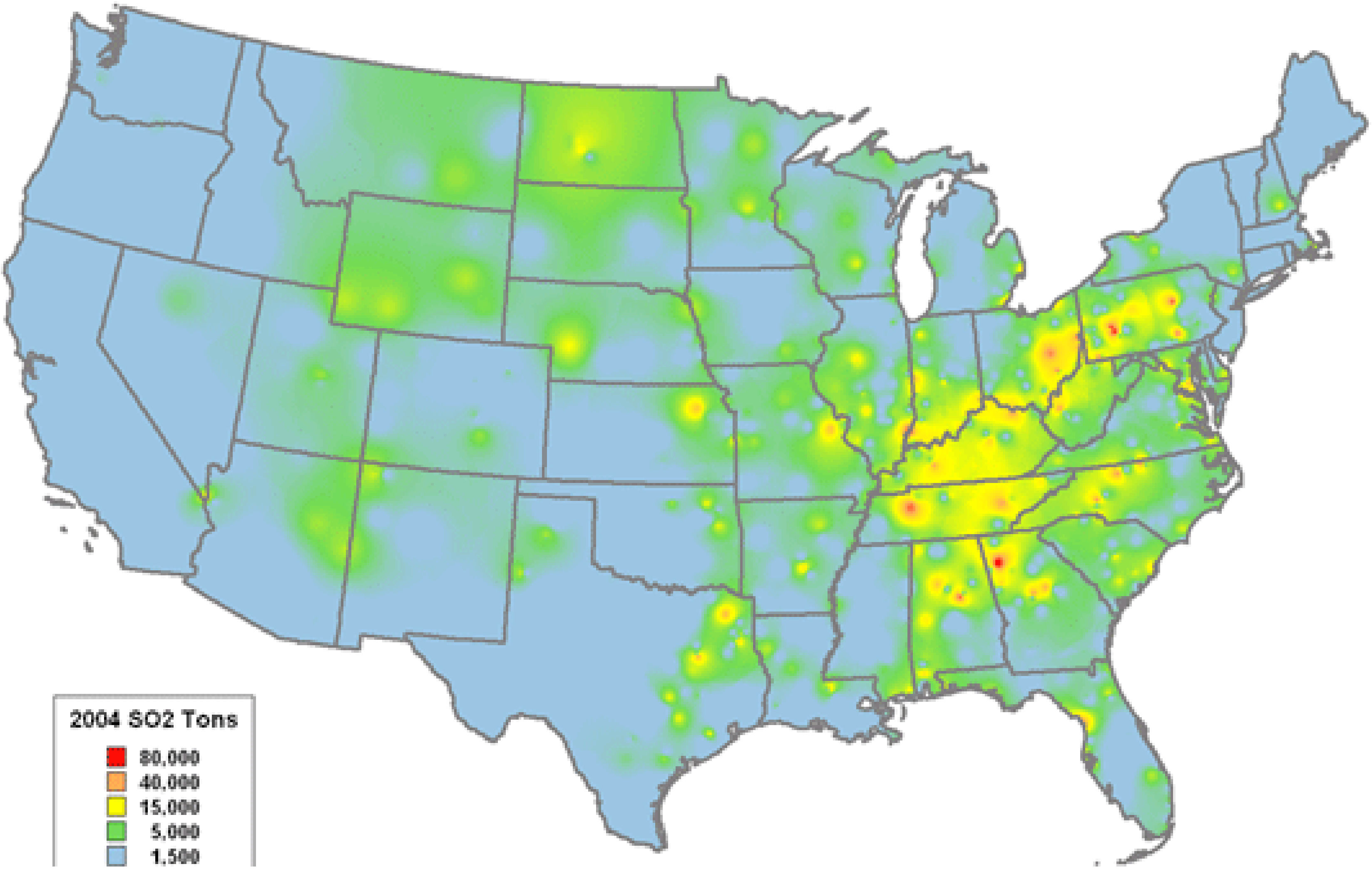


http://www.epa.gov/airmarkets/progress/ARP09_1.html

1995 SO_2 Emissions



2004 SO_2 Emissions



Overall, Title IV Considered Success

- Flexibility: low-S coal, scrubbing, fuel switching, efficiency, conservation;
- Costs << command-and-control
- Benefits >> costs; mostly health-related
- Observed reduction in S deposition, increase in pH, slow recovery of some NE lakes

But additional reductions necessary:

- No recovery, continued acidification of Adirondack lakes, southern Blue Ridge streams
- NO_x more important than originally thought