Chemical Weathering & Acid-Base Reactions

Acid Rain → Focus on Acid Inputs & Determining Factors

- Problems due to the burning of high-sulfur coal have lessened with use of low-sulfur coal. Problem still persists
- Production zones: dominantly in the mid-Eastern States and in Eastern Europe.
- Problem with nitrogen oxides: non-point source –pollution from autos
- The places impacted by the acid rain →Adirondacks, New England, Canadian Shield. (Canadians complain about the amount of S-producing gases moving across their border from the US and polluting their lakes. However, Canada is the largest single point source of S (Sudbury-Nickel smelting)).

Combined emissions of air pollutants in the United States and Canada from various sectors.

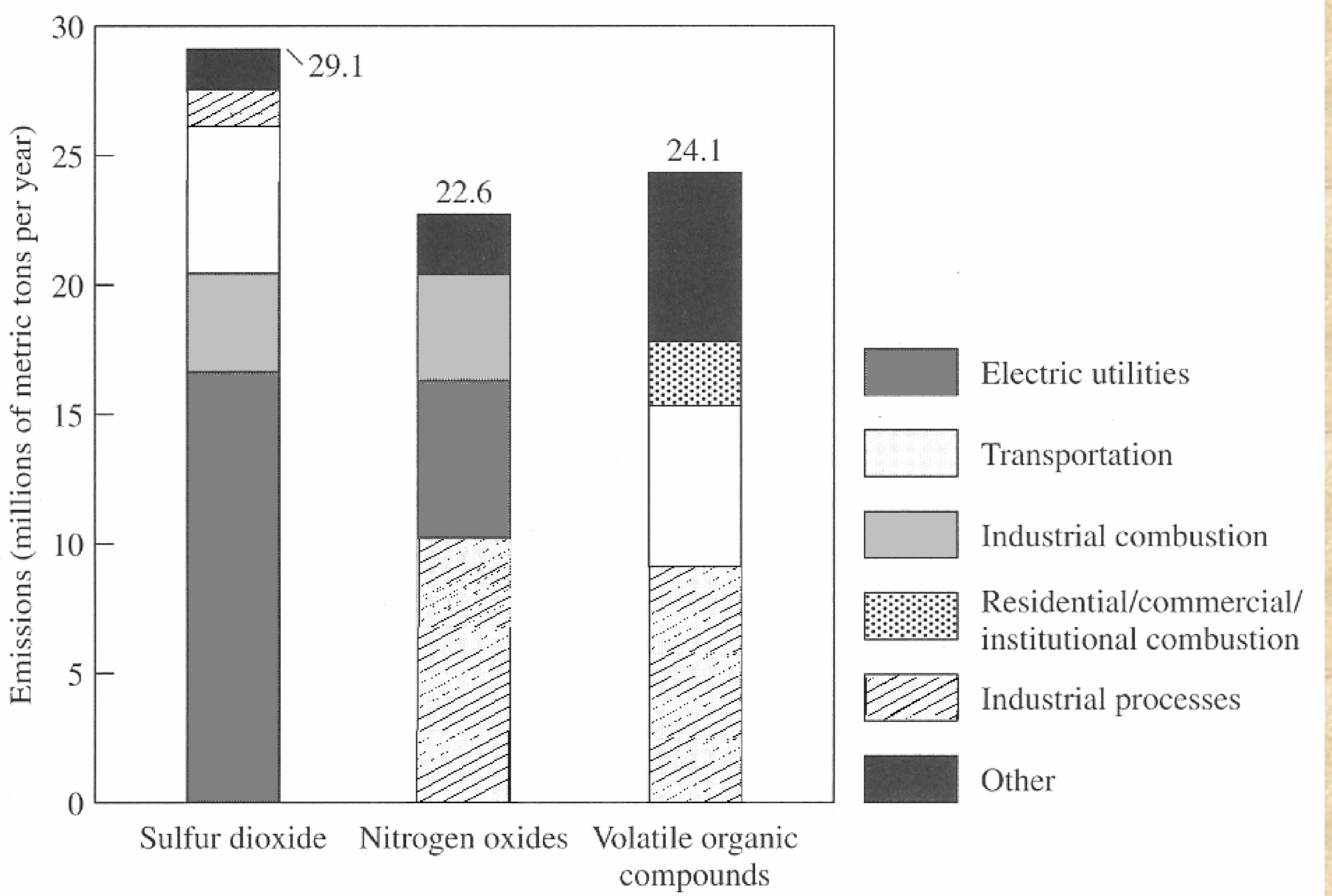
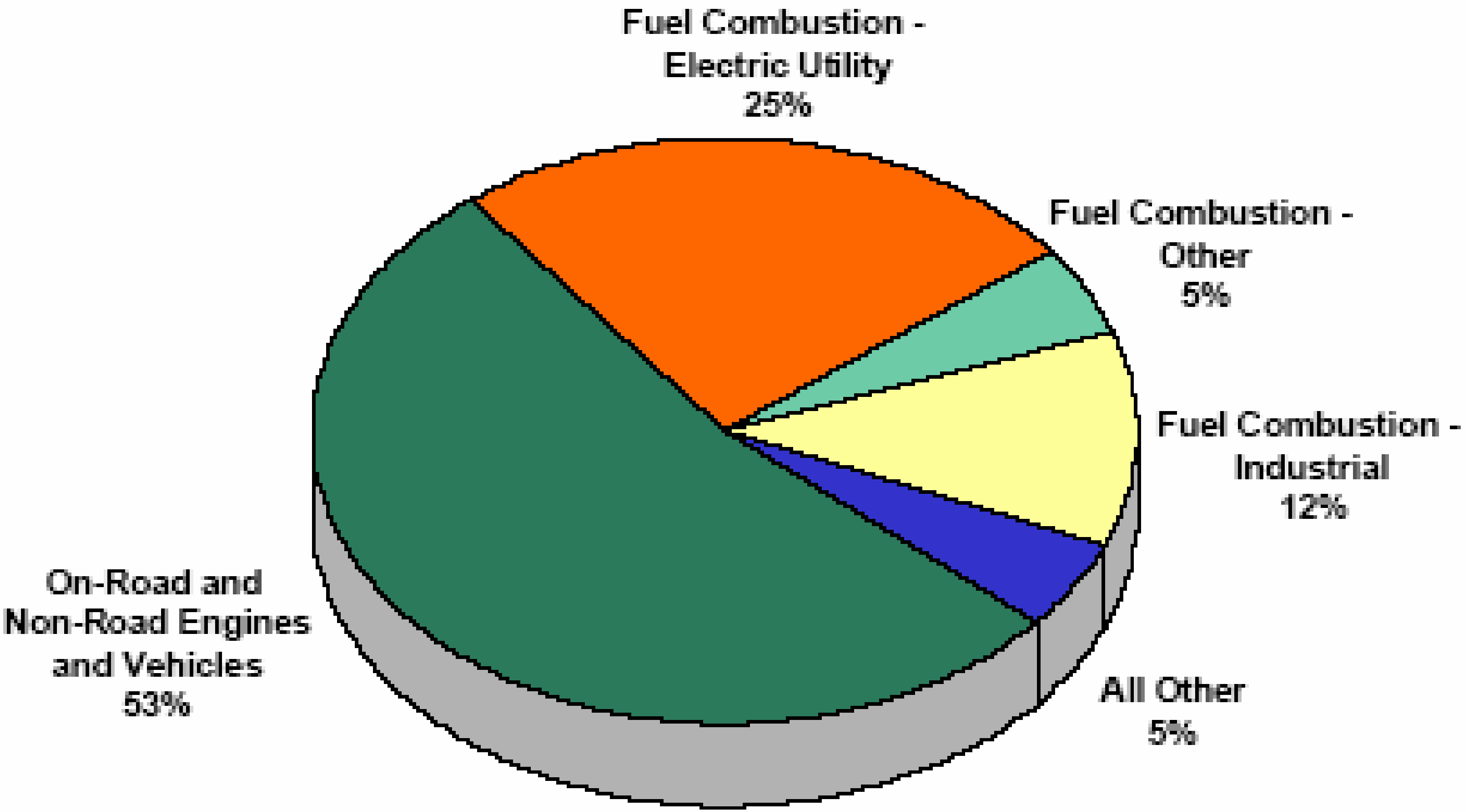


Figure 3-1. Baird. Environmental Chemistry, 1995.

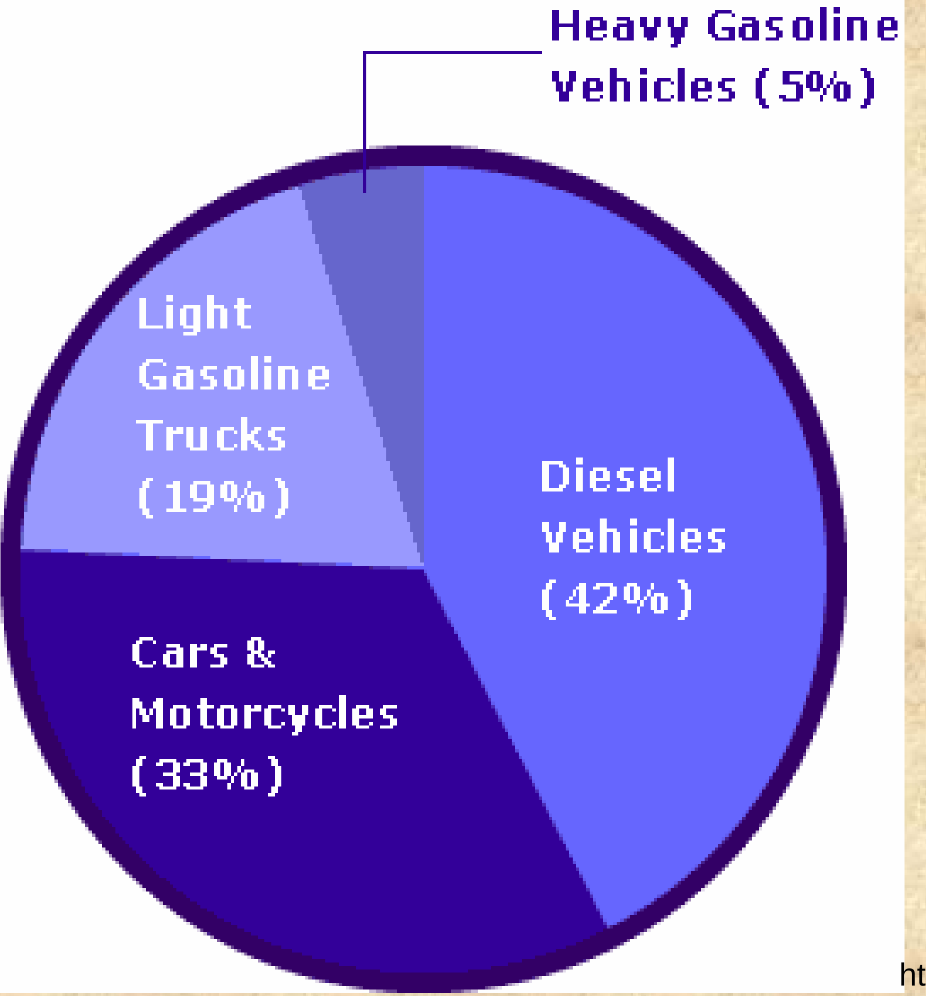
1998 National Nitrogen Oxide (NO_x) Emissions by Principal Source Category



http://www.epa.gov/airmarkets/articles/nitrogen.pdf

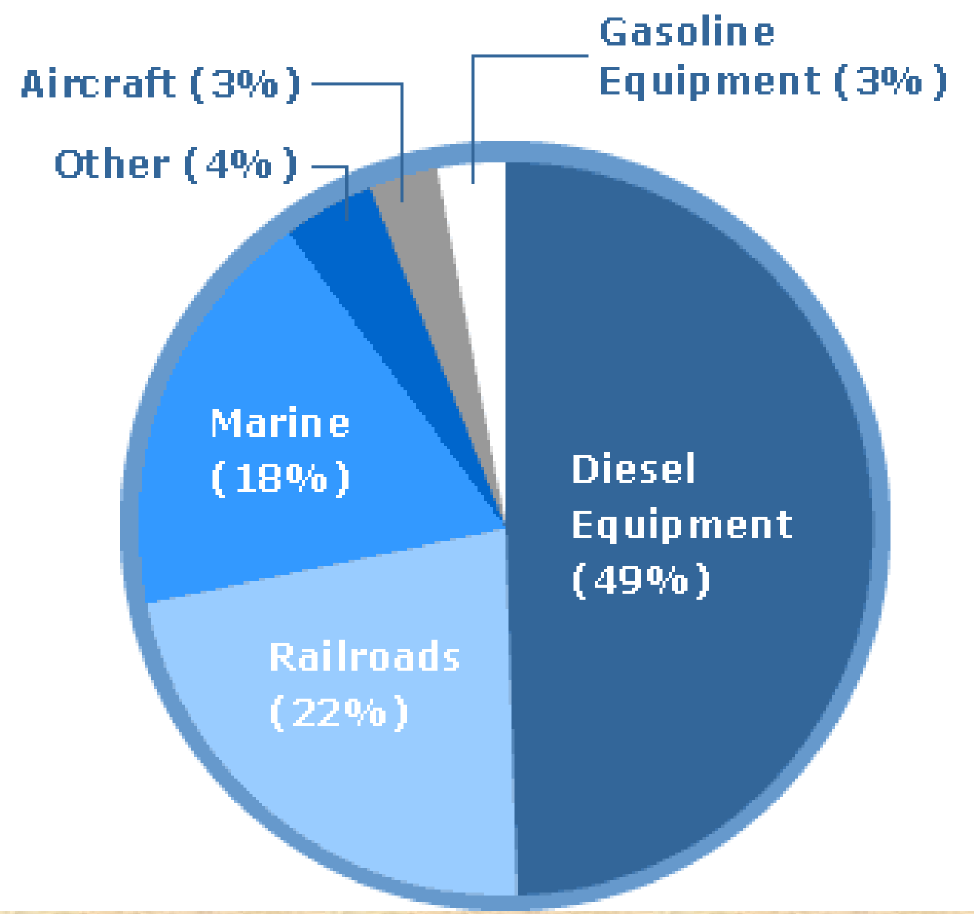
1999 National Emissions by Source: Nitrogen Oxides

On-Road Mobile Sources



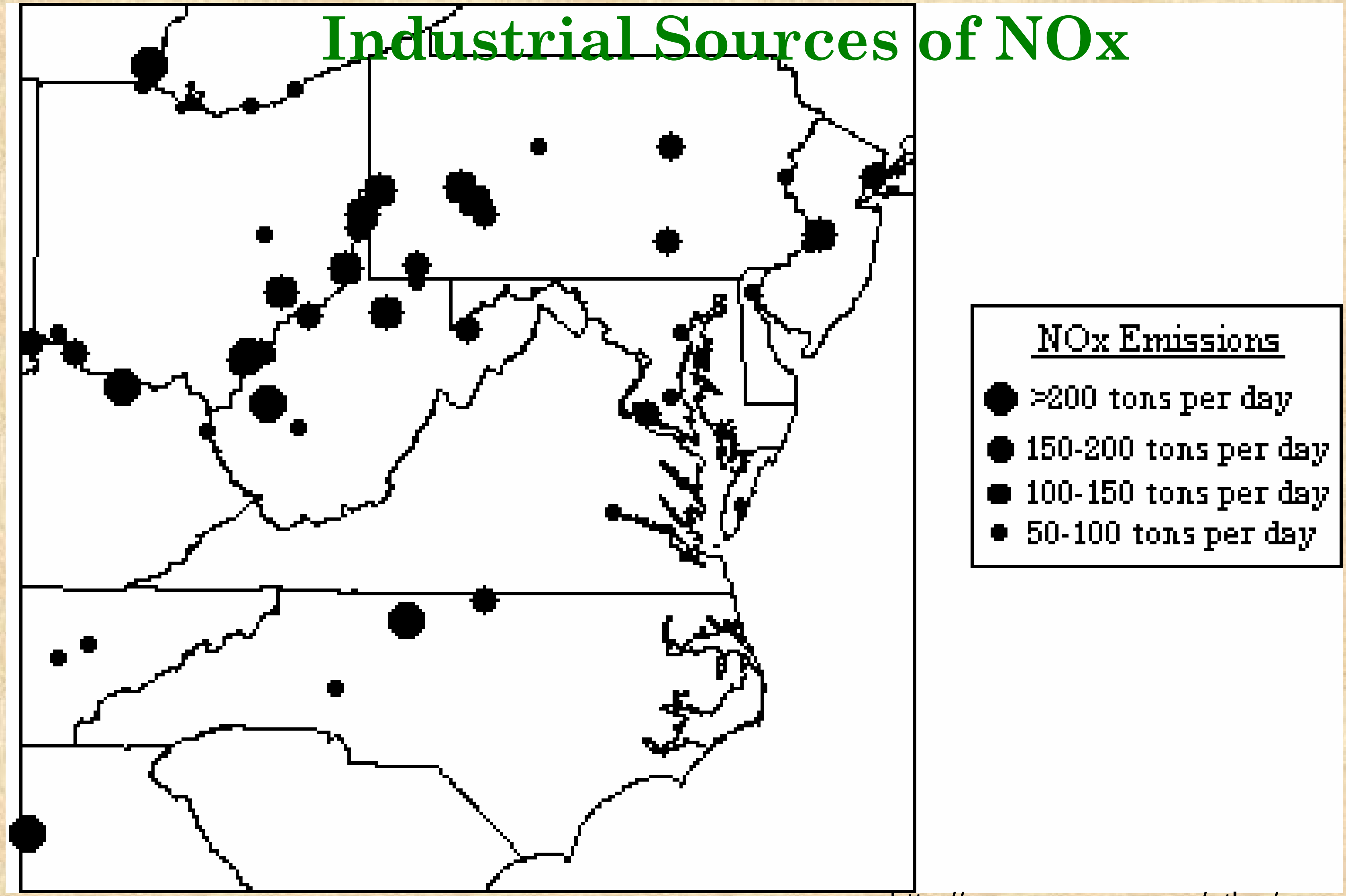
http://www.epa.gov/oms/invntory/overview/pollutants/nox_onroad.htm

Nonroad Mobile Sources



http://www.epa.gov/oms/invntory/overview/pollutants/nox_nonroad.htm

Location of the Largest Utility and Industrial Sources of NOx



http://www.marama.org/atlas/page27.html

Emissions of NO_x in the United States from 1940 - 1980

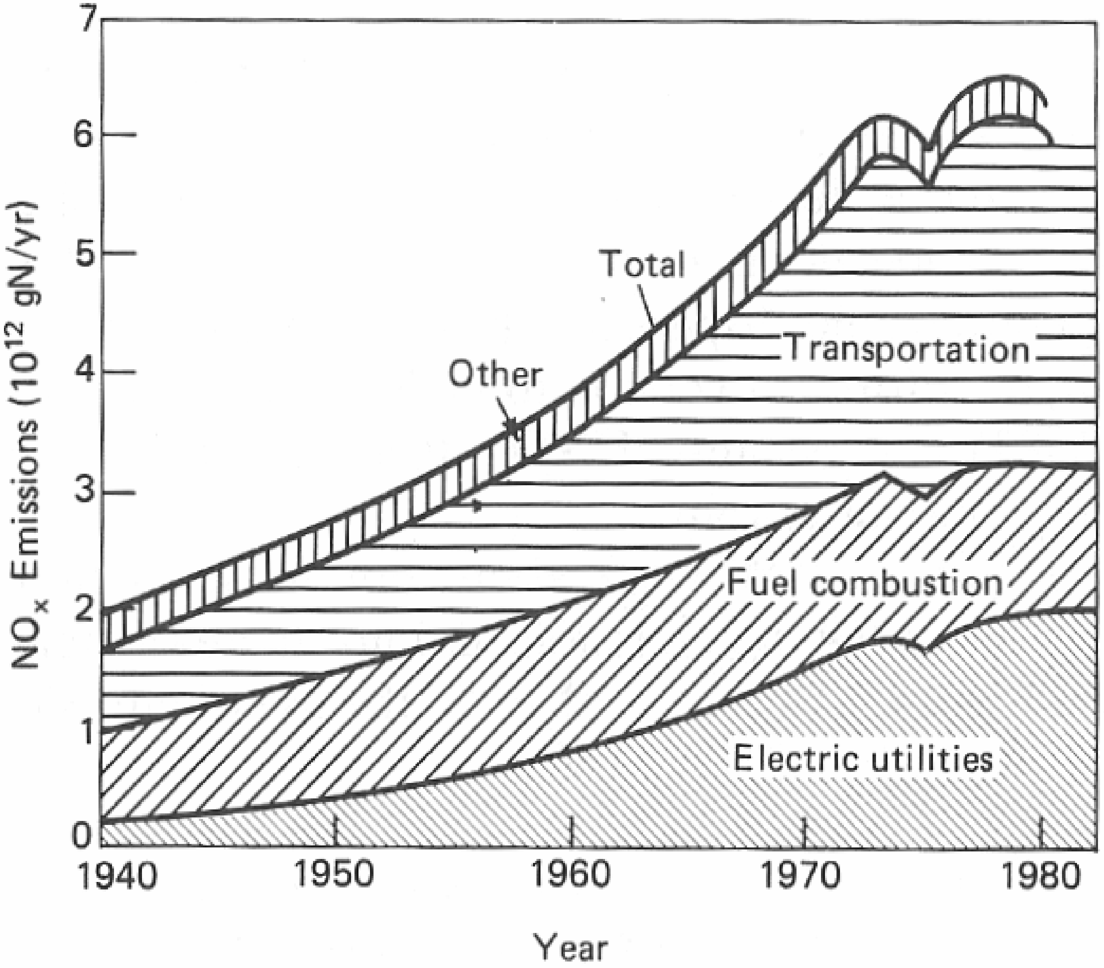
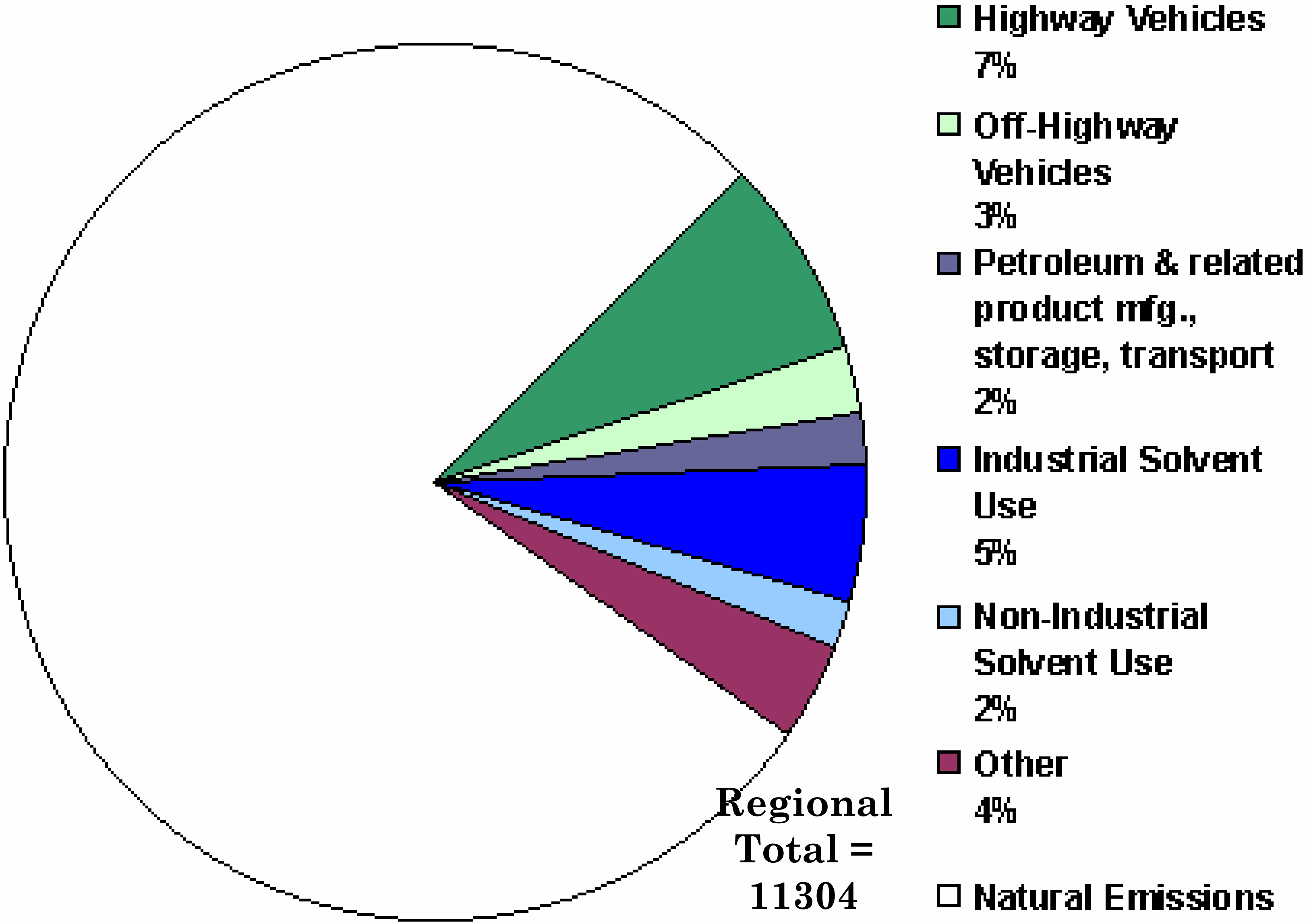


Figure 3.14 Emissions of NO_x in the United States from combustion of fossil fuels and industrial processes in units of 10^{12} g N/yr (10^{12} g N = Tg N). The sources shown separately for 1940 to 1980 are power generation by electric utilities, industrial fuel combustion, transportation combustion and industrial processes ("other"). [J. A. Logan. "Nitrogen Oxides in the Troposphere: global and regional budgets," *J. of Geophysical Research*, 88 (C15), 10790. © 1983 by the American Geophysical Union.] (After U.S. EPA 1982).

Figure 3.14. Berner. *The Global Water Cycle*, 1987

1990 Mid-Atlantic VOC Emissions

Tons per Day (Natural Emissions, 1988)

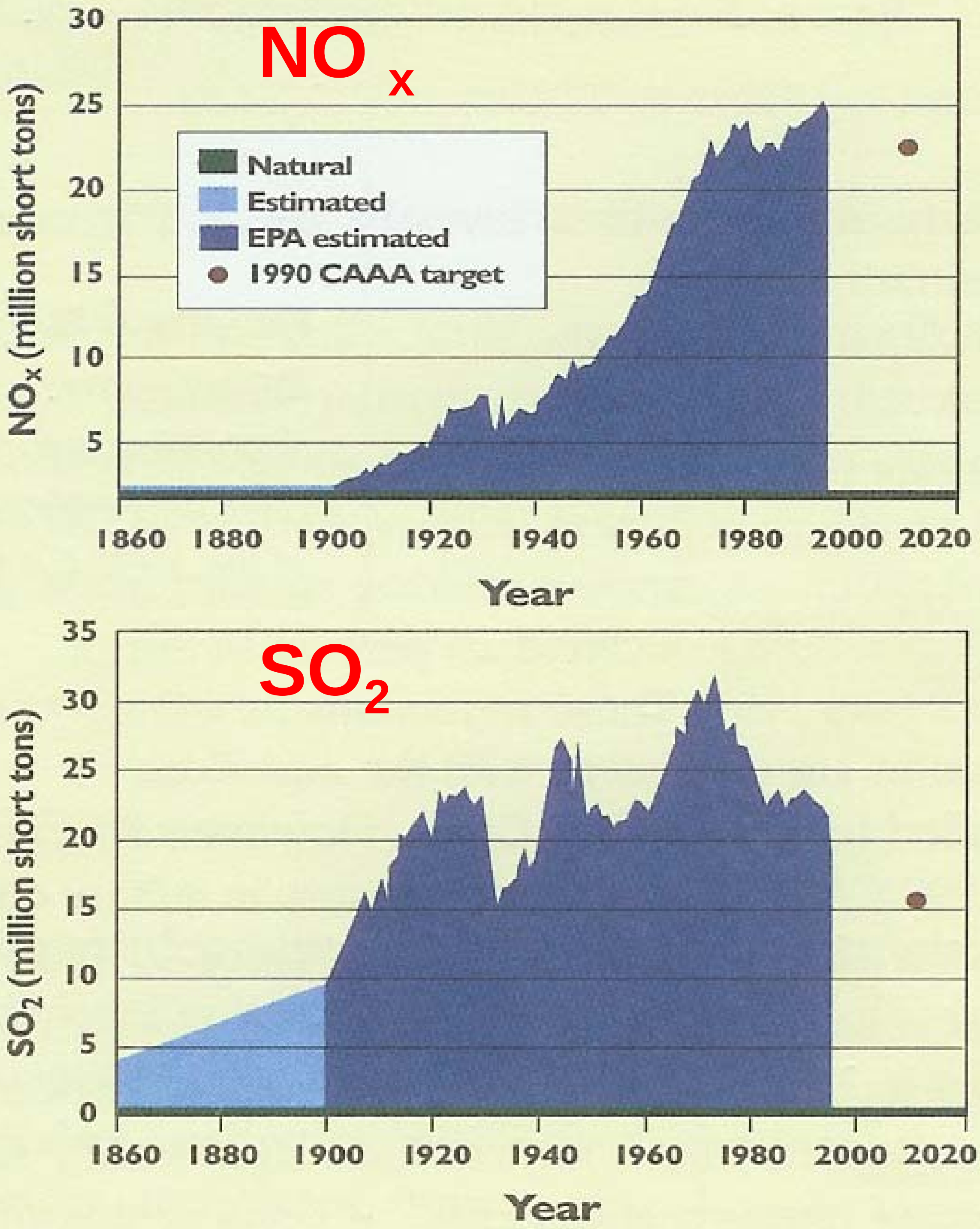


Regional Total = 11304 tons/day

http://www.marama.org/atlas/page29.html

Source: EPA (1996)

Total US Emissions



Long-term trends in total nitrogen oxide and sulfur emissions in the United States compared with estimated natural emissions and emission targets estimated based on the 1990 CAAA (after U.S. EPA 2000)

Figure 4. “Acid Rain Revisited.” HBRF

Rise in emissions of SO_2 and NO_x from 1940 to 1980

Figure 3.9. Berner. *The Global Water Cycle*, 1987.

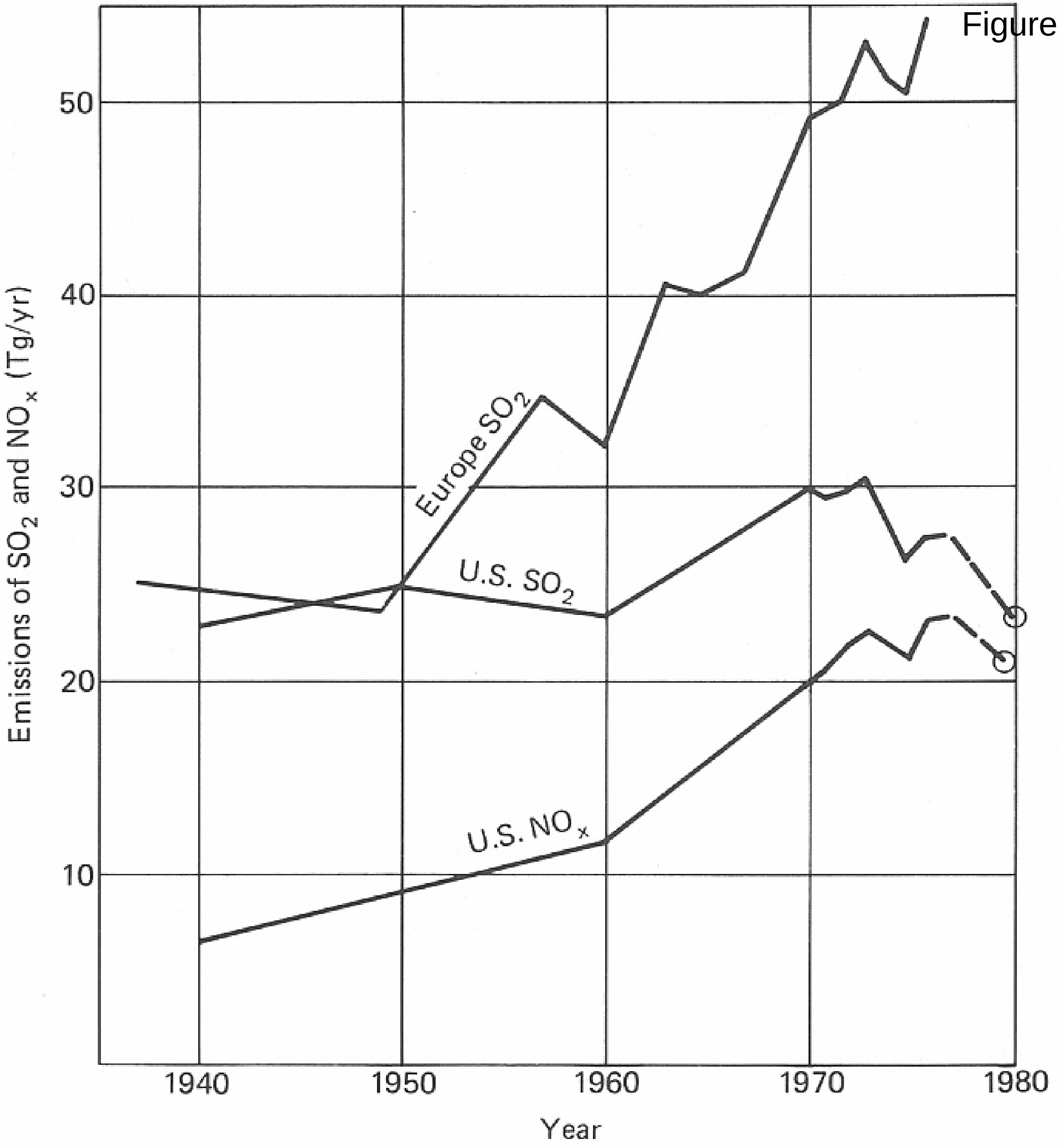
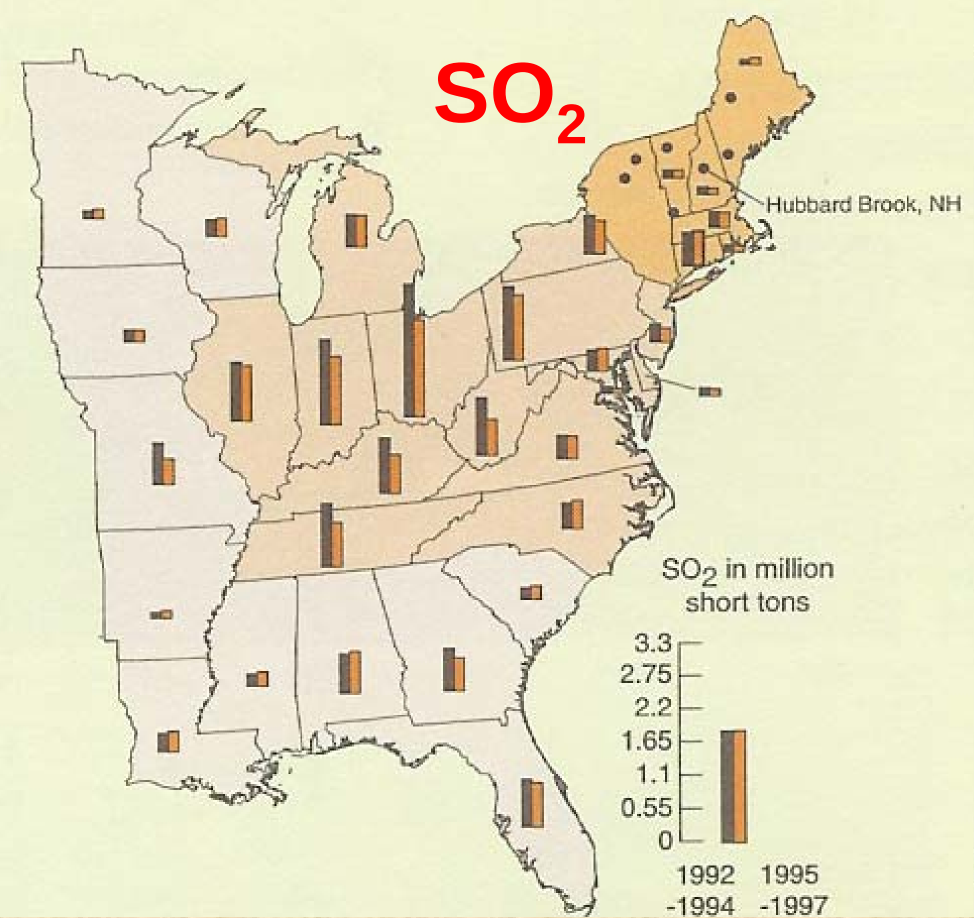
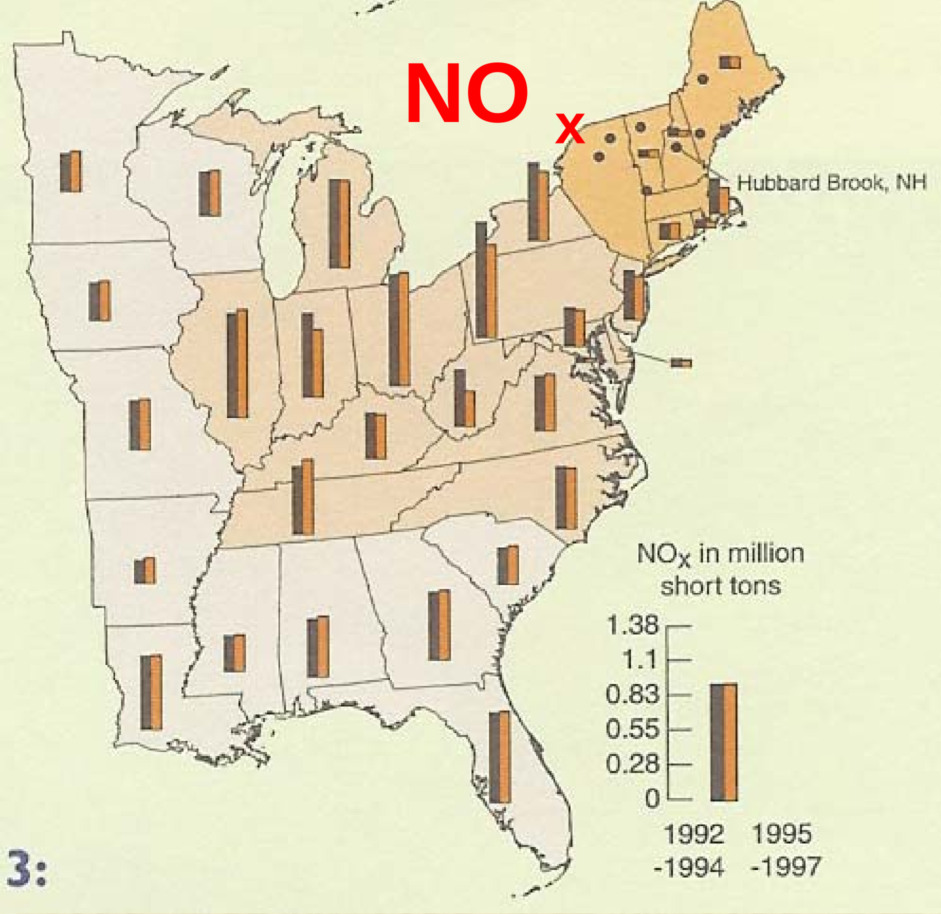


Figure 3.9 Rise in emissions of SO_2 and NO_x from 1940 to 1980. Top curve: European SO_2; middle curve: U.S. SO_2; bottom curve: U.S. NO_x. To compare SO_2 data here with data given elsewhere in the present chapter, divide by 2 to obtain Tg S/yr. 1980 U.S. SO_2 emissions from Marshall 1983; 1979 U.S. NO_x emissions from Logan 1983 [see also Table 3.16].(From G. E. Likens et al., "Acid Rain." Copyright © October 1979 by Scientific American, Inc. All rights reserved.)



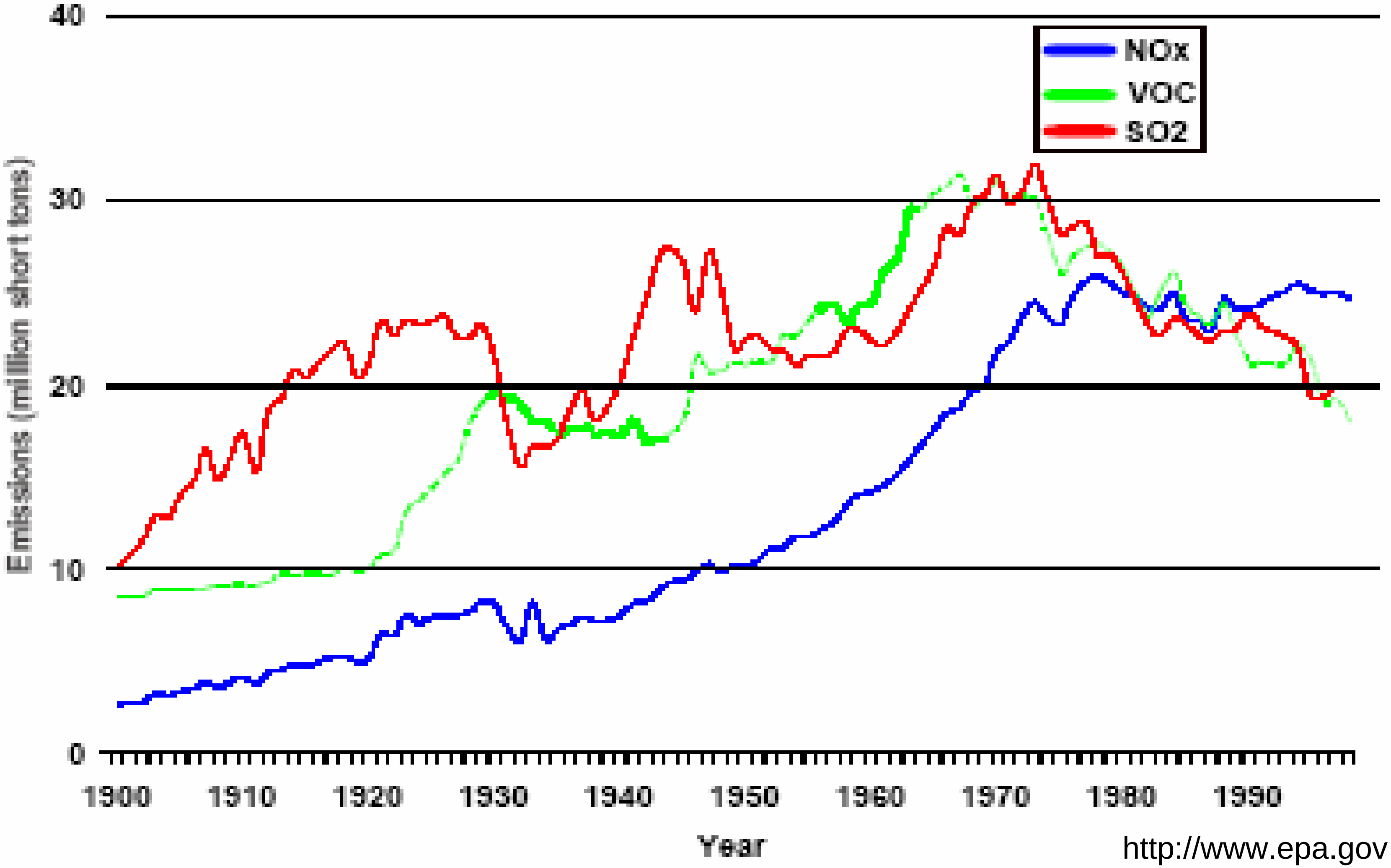
Spatial patterns of sulfur dioxide emissions in the eastern United States. The shaded area shows the source area from which pollution travels downwind to the Northeast.



Spatial patterns of nitrogen oxide emissions in the eastern United States. The shaded area shows the source area from which pollution travels downwind to the Northeast.

Figure 3. “Acid Rain Revisited.” HBRF

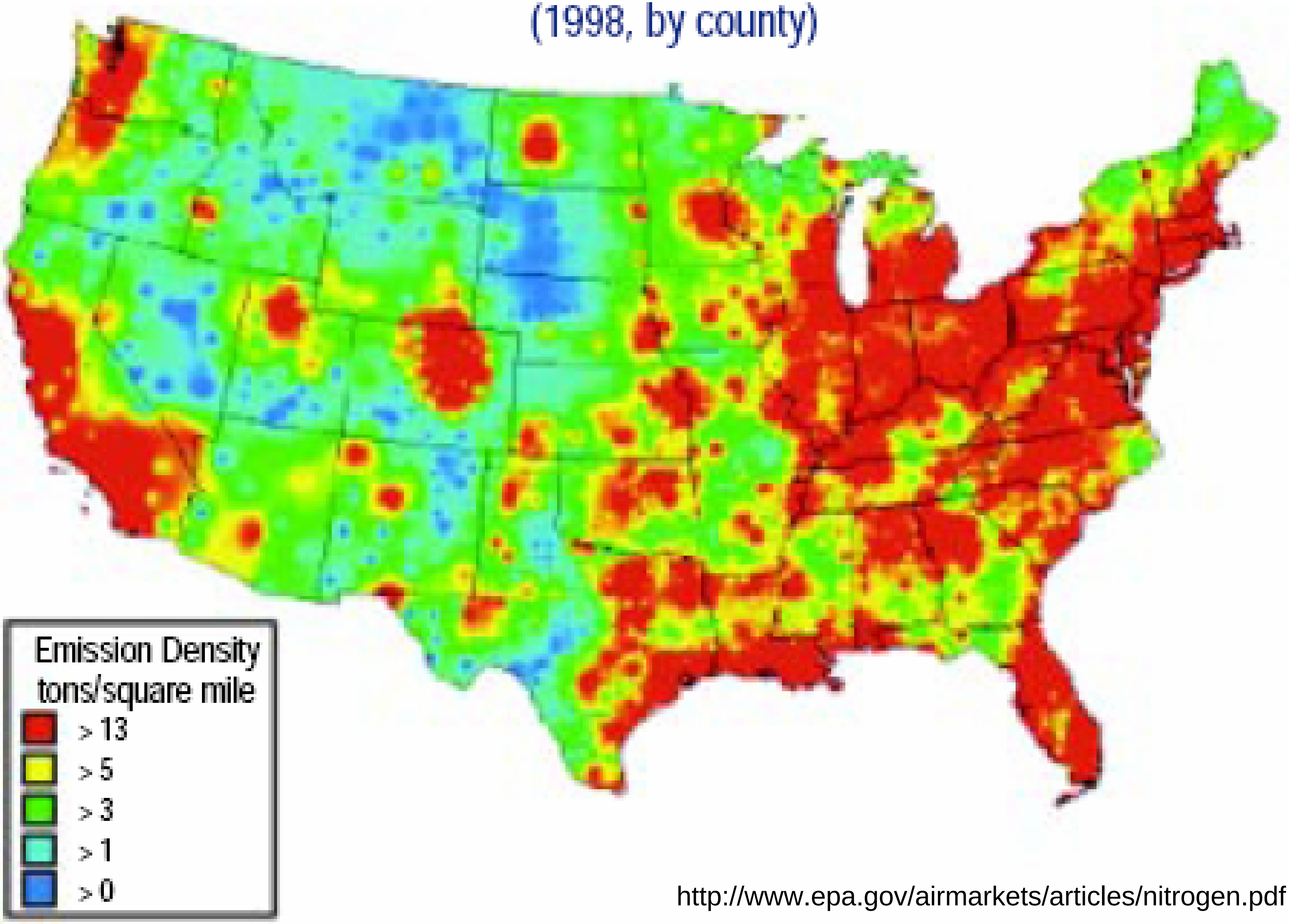
Trends in National Emissions of Nitrogen Oxides, Volatile Organic Compounds, and Sulfur Dioxide, 1900-1998



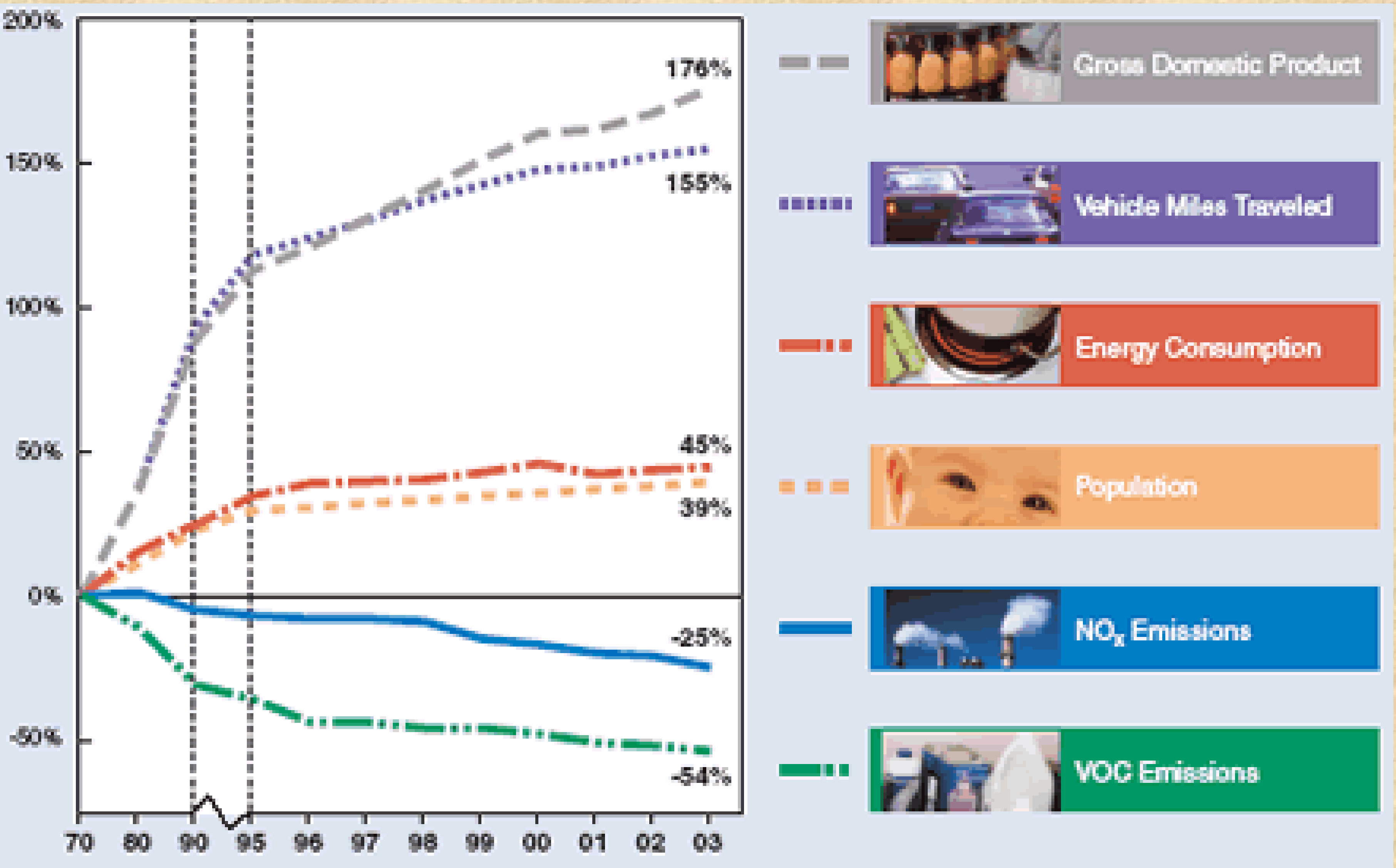
http://www.epa.gov

U.S. Emissions of NO_x

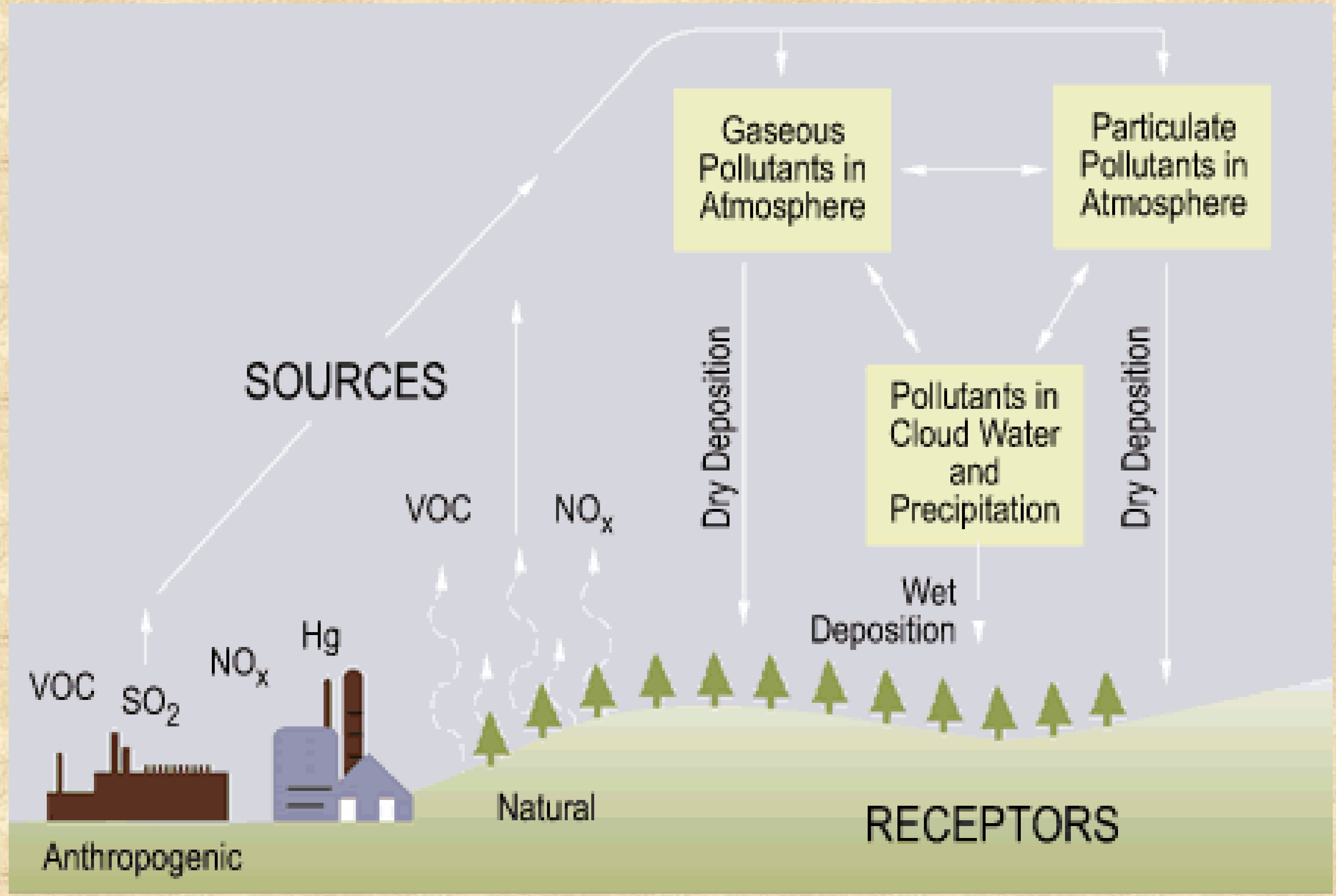
(1998, by county)



http://www.epa.gov/airmarkets/articles/nitrogen.pdf

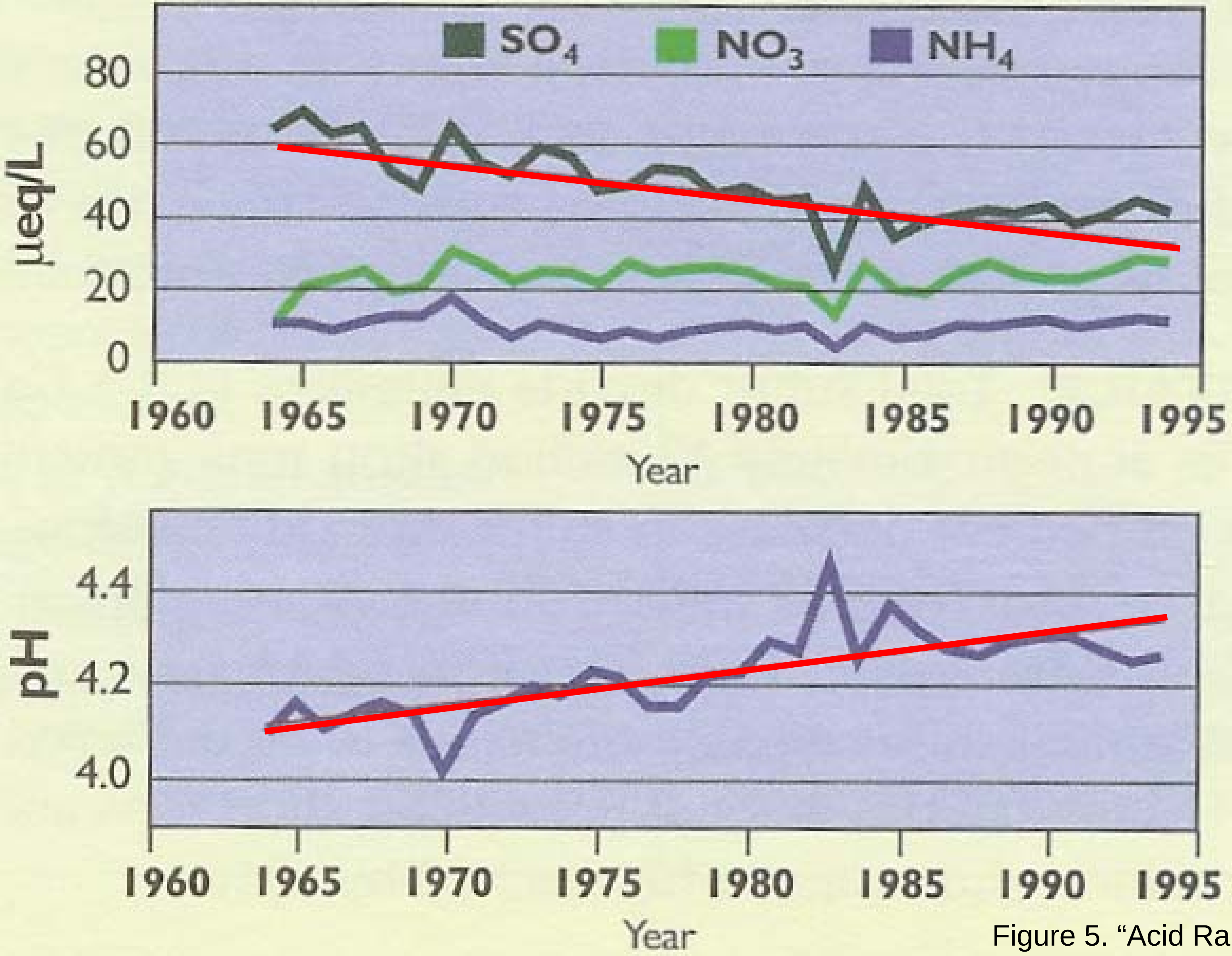


http://www.epa.gov/airtrends/2003ozonereport/lookat2003.html



http://www.epa.gov

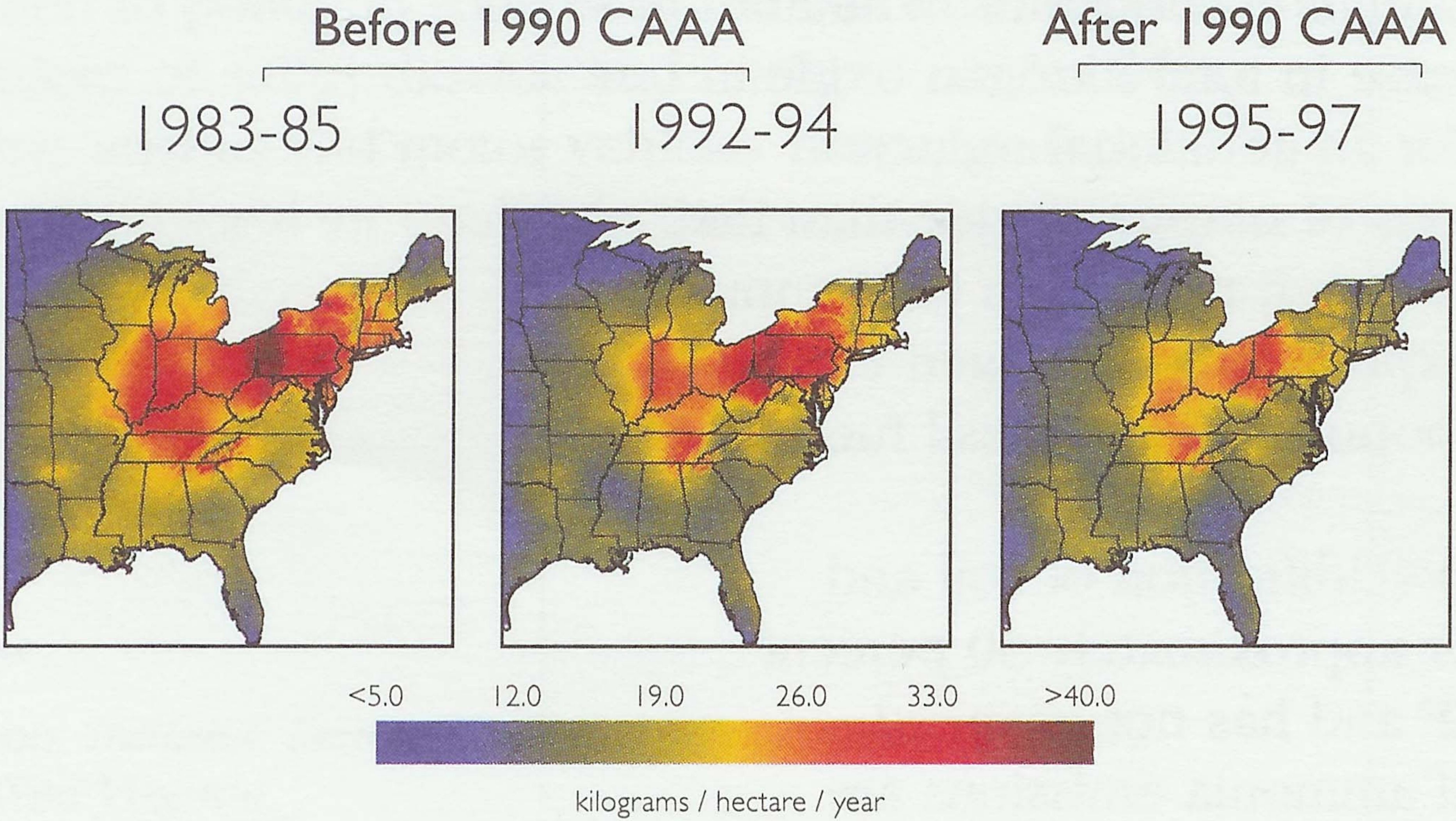
LONG-TERM TRENDS IN WET DEPOSITION



Long-term trends in sulfate, nitrate, and ammonium concentrations and pH in wet deposition at the HBEF, 1963-1994. The solid lines indicate statistically significant trends.

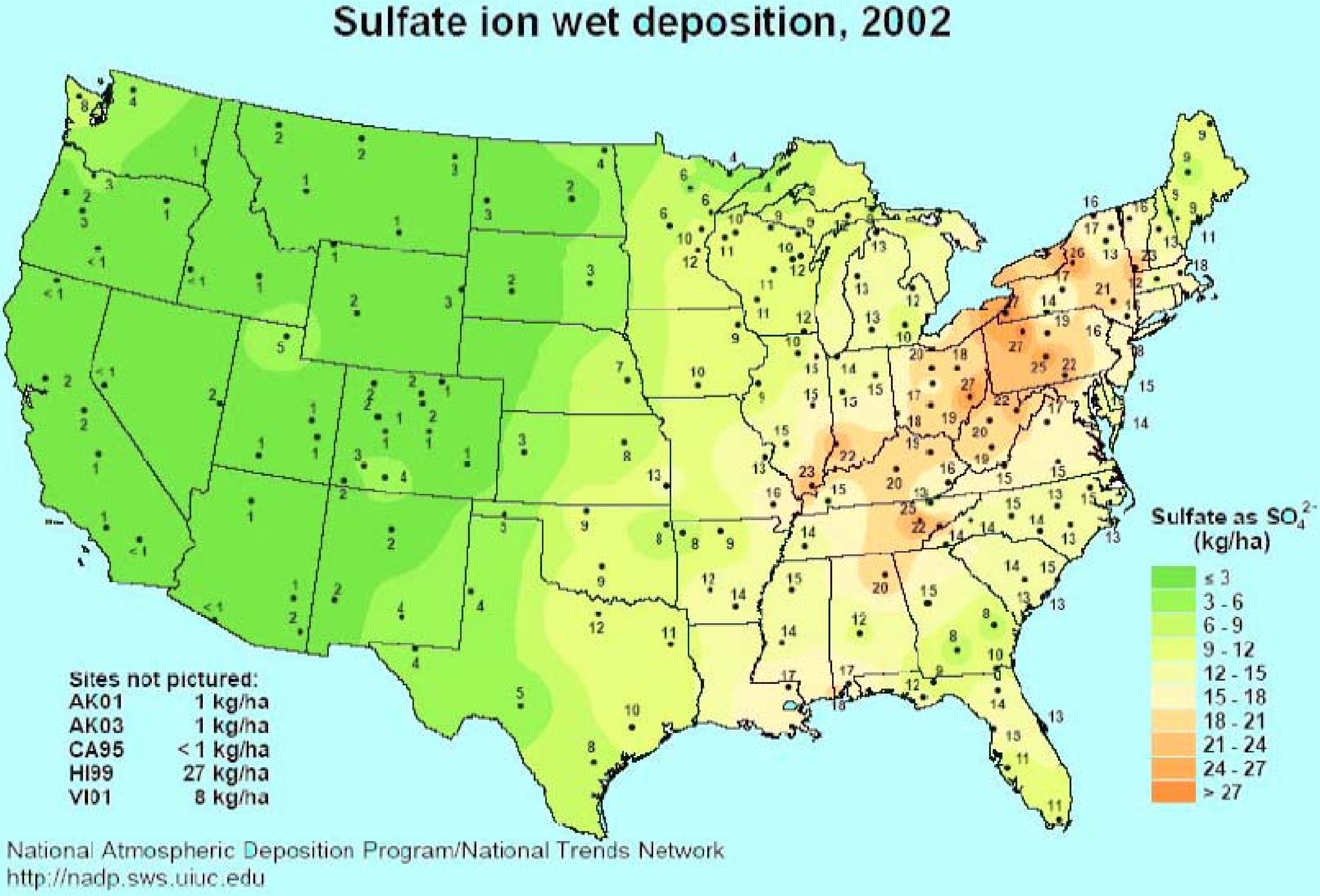
Figure 5. “Acid Rain Revisited.” HBRF

Sulfate Wet Deposition



Annual wet deposition of SO_4^{2-} (in kg $SO_4^{2-} \cdot ha^{-1} \cdot yr^{-1}$) in the eastern United States for 1983-1985, 1992-1994, 1995-1997.

Figure 4. Driscoll et al. “Acid Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies

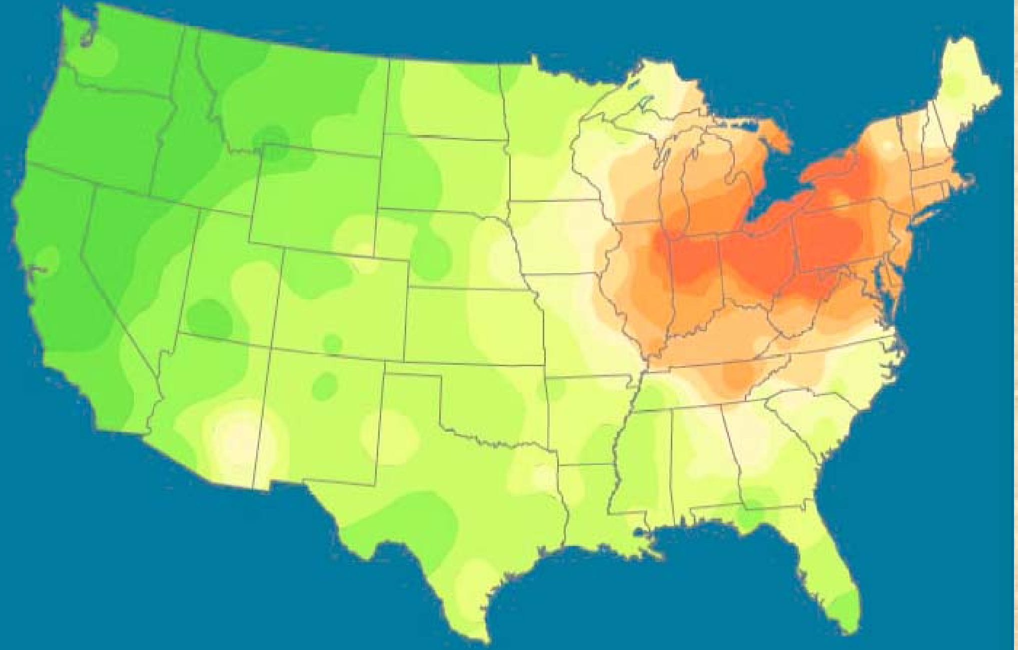


Sites not pictured:

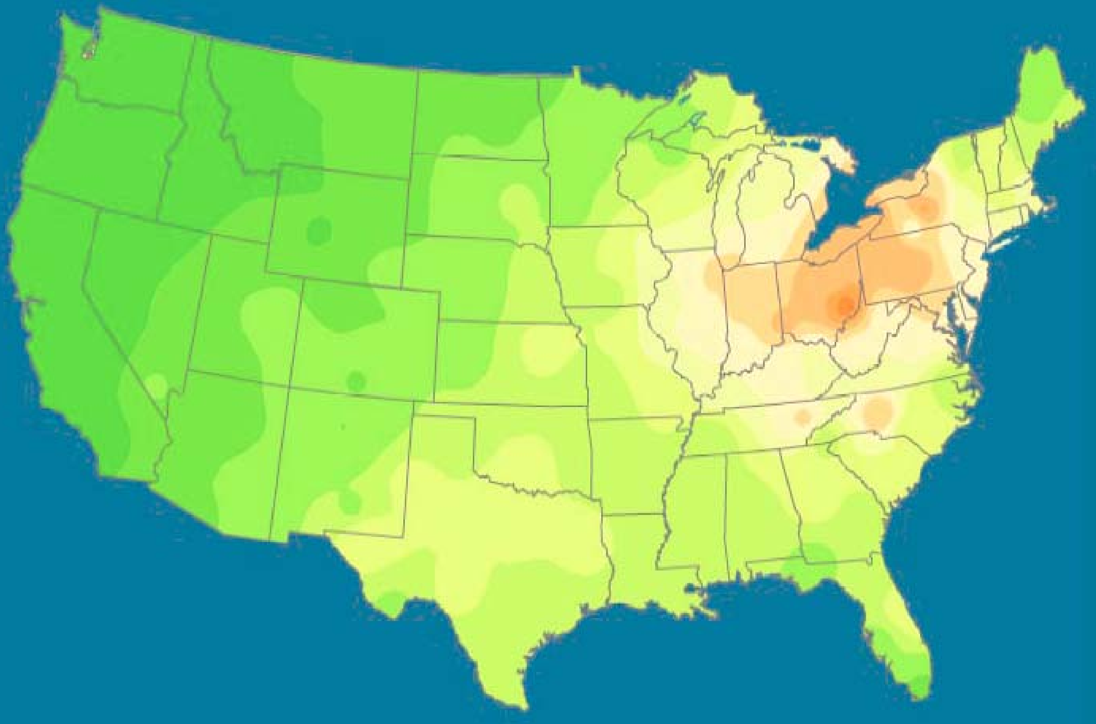
AK01	1 kg/ha
AK03	1 kg/ha
CA95	< 1 kg/ha
HI99	27 kg/ha
VI01	8 kg/ha

Nilles, “Status and Trends in Wet Deposition of Sulfur and Nitrogen in the United States,” USGS.

Sulfate Ion Concentrations



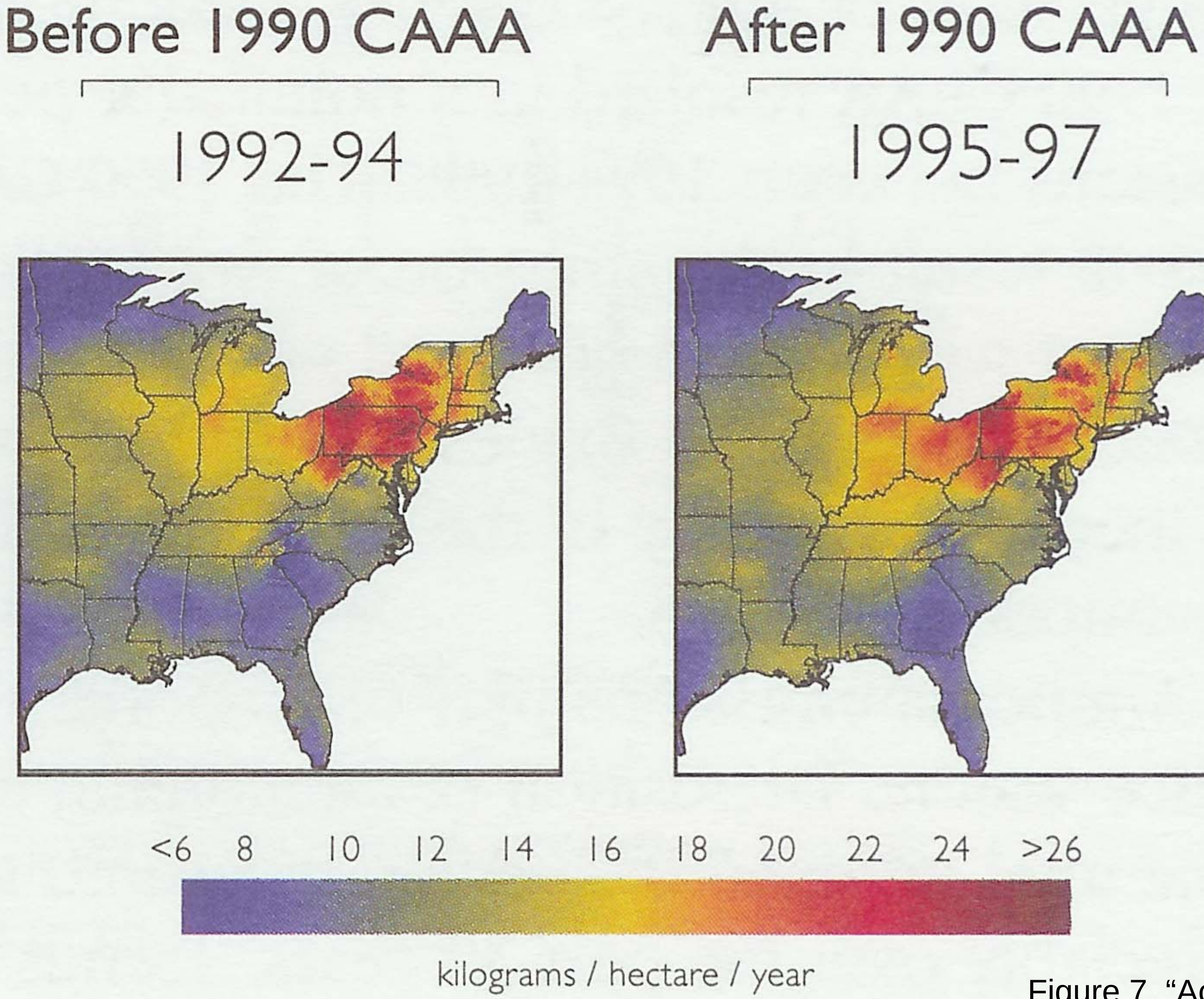
← 1984-1986



← 1999-2001

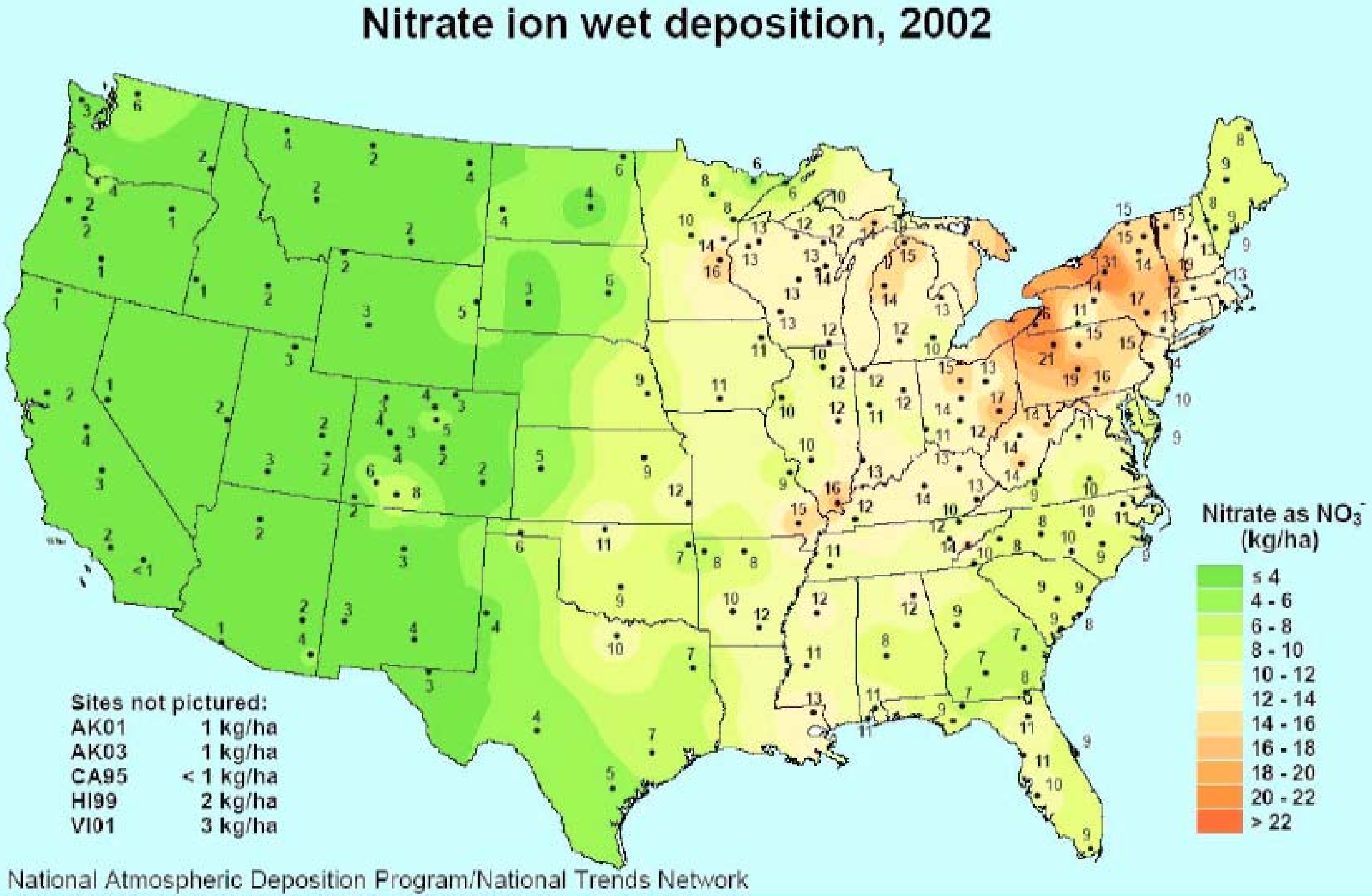
Nilles, “Status and Trends in Wet Deposition of Sulfur and Nitrogen in the United States,” USGS.

NITRATE WET DEPOSITION



Recent patterns of wet deposition before and after the implementation of 1990 CAAA. Note: 1 hectare equals 2.47 acres.

Figure 7. “Acid Rain Revisited.” HBRF



Nitrate ion wet deposition, 2002

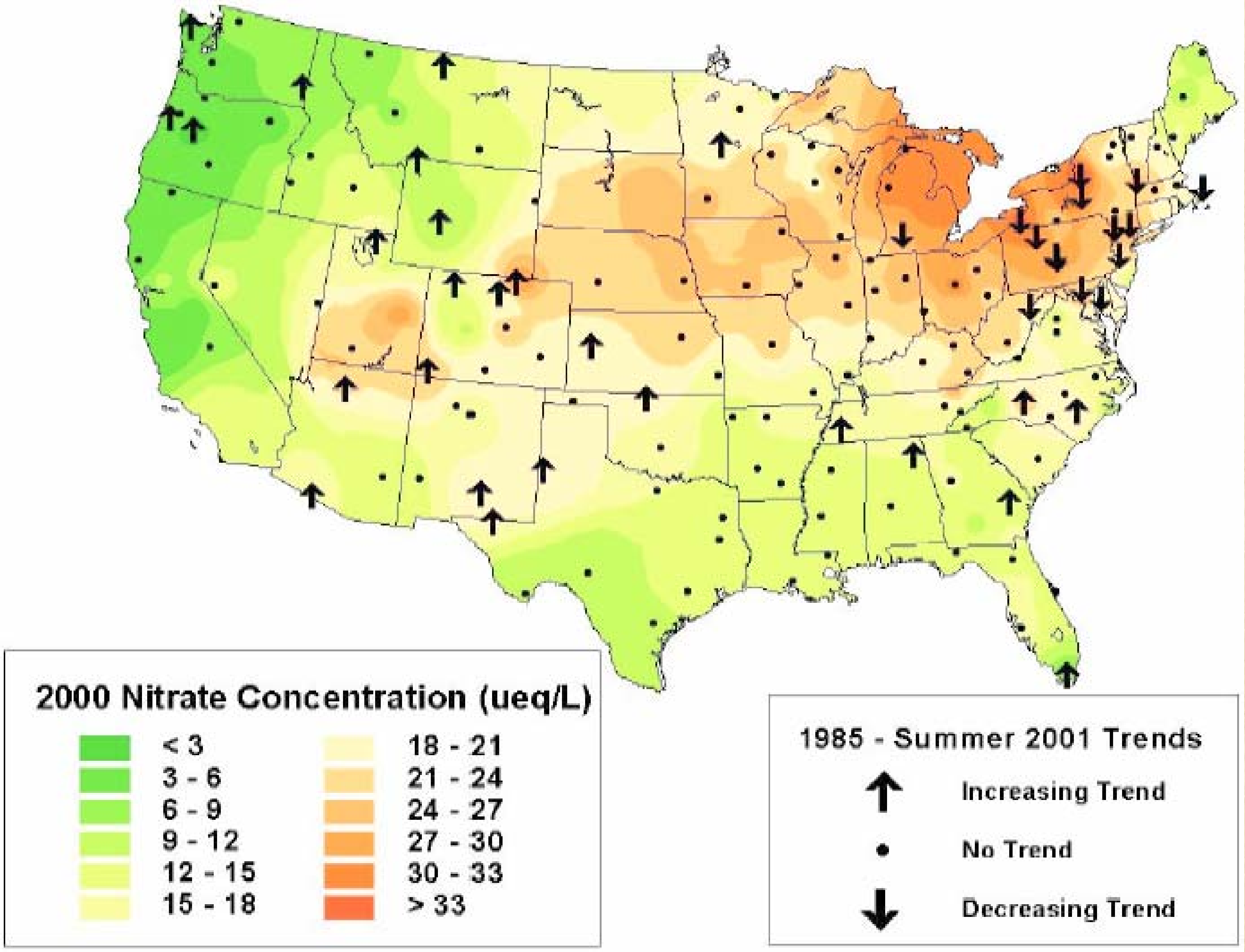
Sites not pictured:

AK01	1 kg/ha
AK03	1 kg/ha
CA95	< 1 kg/ha
HI99	2 kg/ha
VI01	3 kg/ha

National Atmospheric Deposition Program/National Trends Network

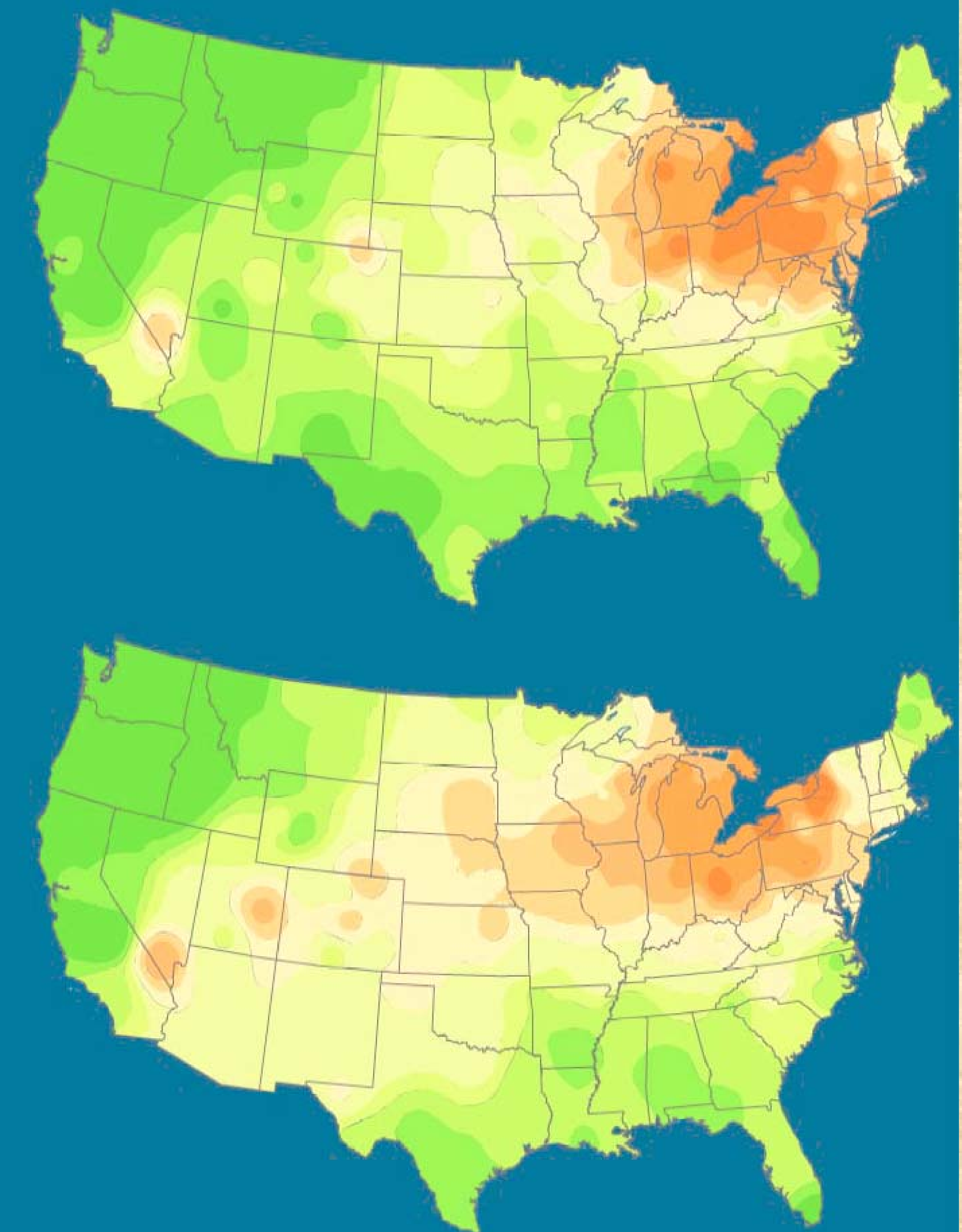
Nilles, “Status and Trends in Wet Deposition of Sulfur and Nitrogen in the United States,” USGS.

Nitrate Trends in Precipitation, 1985-2001



Nilles, "Status and Trends in Wet Deposition of Sulfur and Nitrogen in the United States," USGS.

Nitrate Ion Concentrations

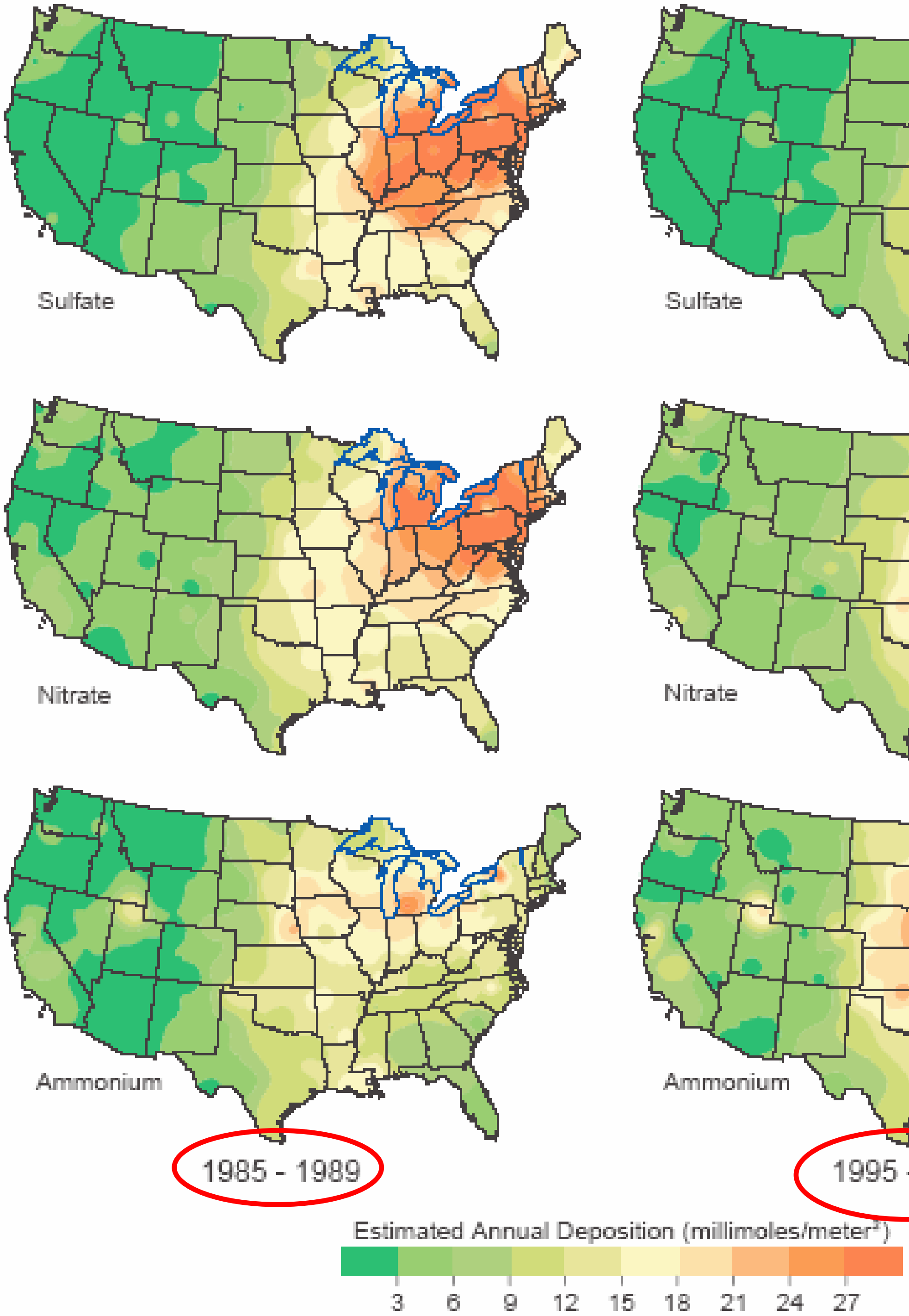


← 1984-1986

← 1999-2001

Nilles, “Status and Trends in Wet Deposition of Sulfur and Nitrogen in the United States,” USGS.

Estimated Annual Wet Deposition: 1985-1999



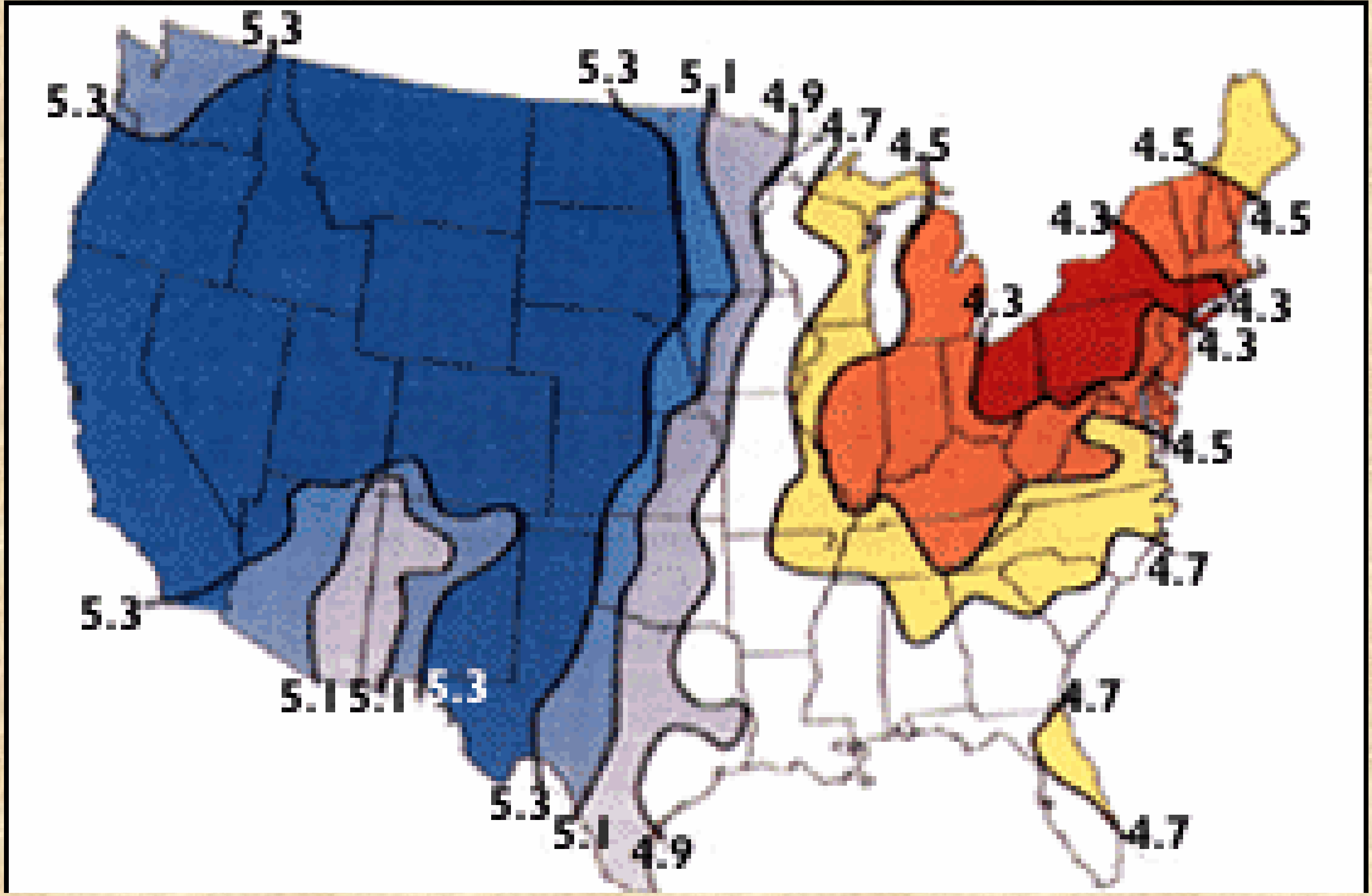
← Sulfate

← Nitrate

← Ammonium

http://www.epa.gov/airmarkets/articles/nitrogen.pdf

1992 Annual precipitation-weighted mean hydrogen ion concentration as pH



http://pubs.usgs.gov/gip/acidrain/gifs/fig04.gif

Aqueous Geochemistry and Weathering

- Weathering is the interaction of water and rock at low temperatures. This will determine the composition of the surrounding waters, such as a river, which will in turn effect to type and rate of weathering.
- Weathering → Water-Rock Interaction at low temperatures → controls Composition of waters.
- What governs weathering reactions?
  - Composition of the rocks.

- Since the affected areas are of metamorphic, igneous rocks, then what happens in reactions associated with metamorphic and igneous rocks?
- Metamorphic, Igneous → 500°C - 1200°C
- 8 Groups of minerals (all silicates)

Least stable	Mafic (Fe, Mg)	Felsic (Na, K, Ca)
Highest		
temperature	**Olivine** $(Fe,Mg)_2SiO_4$	**Plagioclase** (Ca, Na)
of formation	**Pyroxenes** $(Fe, Mg)SiO_3$	**K- Feldspar** $(KAlSi_3O_8)$ *
	Amphiboles (structurally complex)	
Most stable	**Biotite (mica)**	**Quartz** (SiO_2)
Lowest		**Muscovite (mica)**
temperature		
of formation		

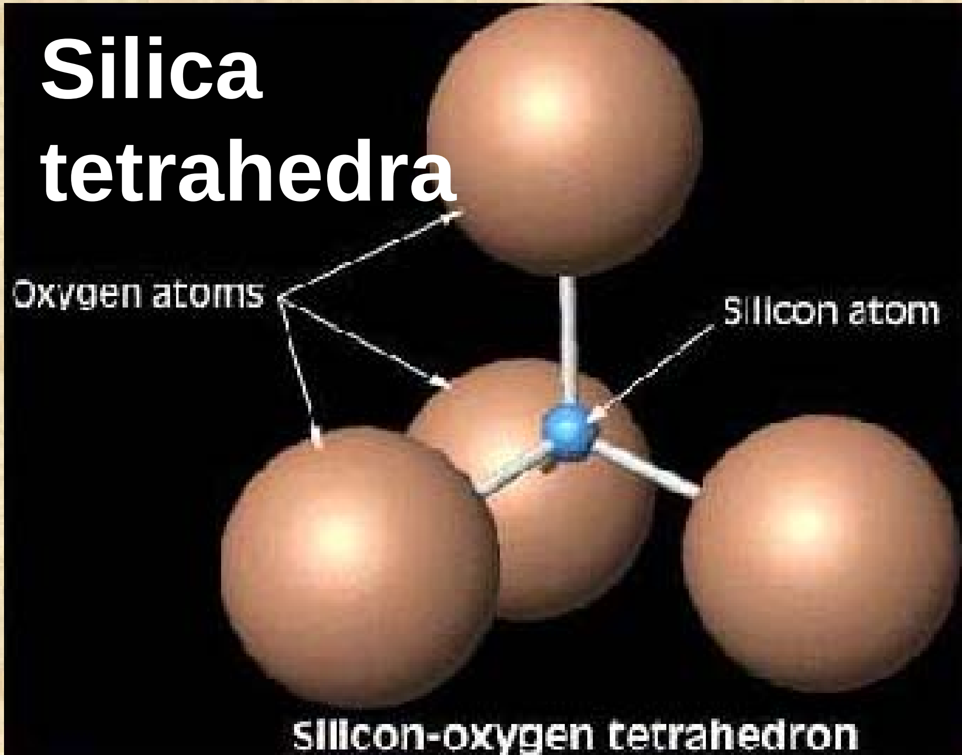
*****(Ca Al silicate - Al is substituting for Si in tetrahedra, great deal of substitution in this system).

All are silicates - formed by silica tetrahedra→ SiO_4^{4-}

Different compositions → different structures

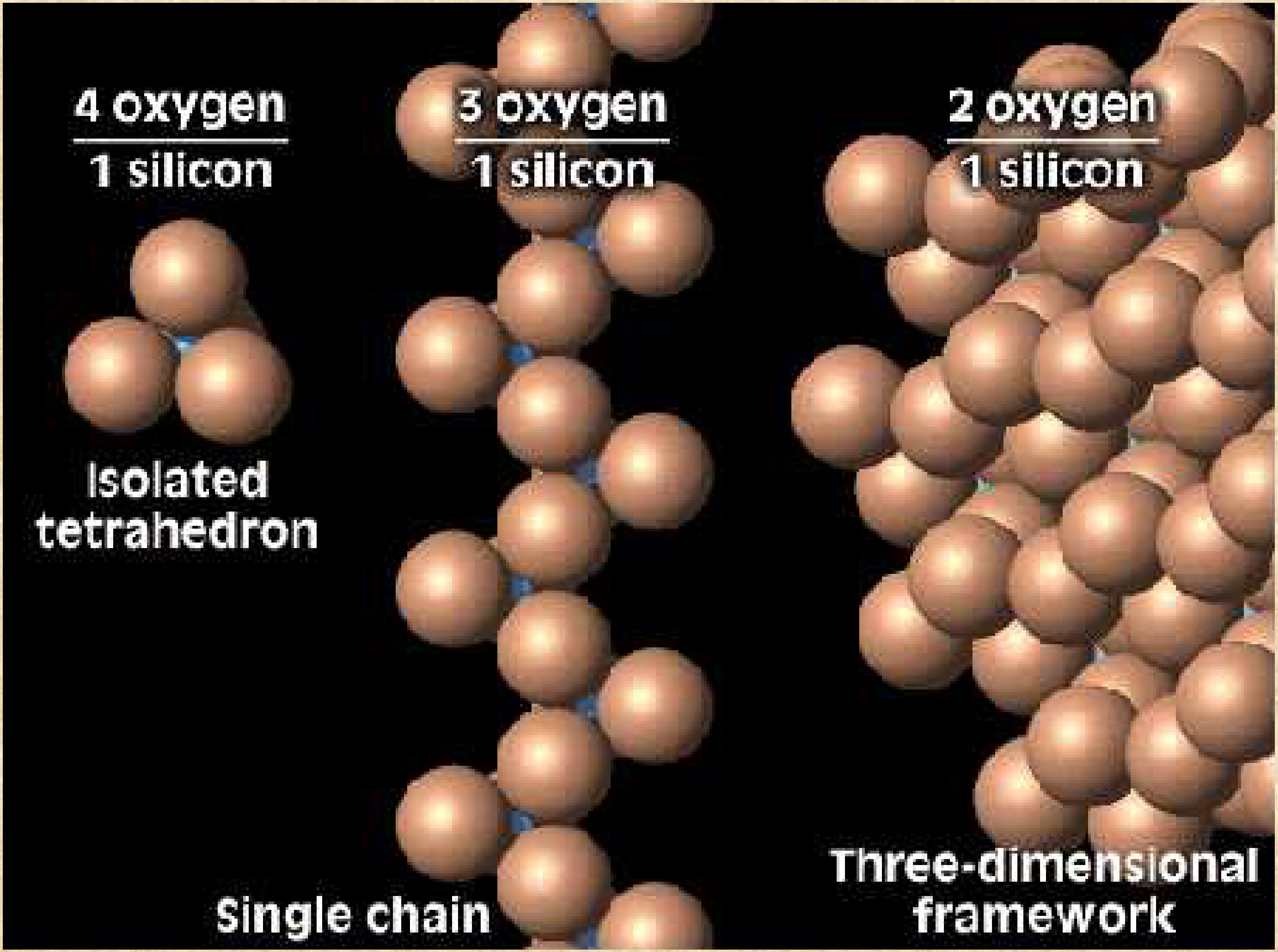
- Al $^{3+}$, Si^{4+} are common ions in tetrahedra (Al will sometimes substitute for Si).
- **Fe^{2+}, *Mg^{2+}, Na^{+}, K^{+}, Ca^{2+}*** all represent base cations (except Fe^{2+})

Mafic Felsic



http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

Oxygen/ Silicon ratios in Silicates



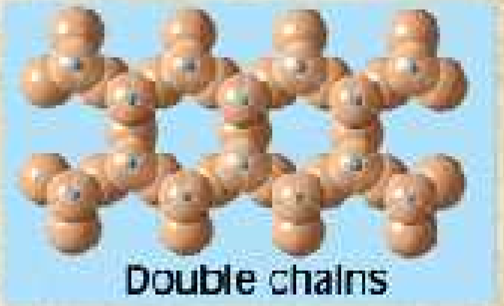
http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld038.htm

Silicate Examples

- Single tetrahedron: Olivine
  - No cleavage; fracture

- Single chains: Pyroxenes
  - Two planes @ 90°

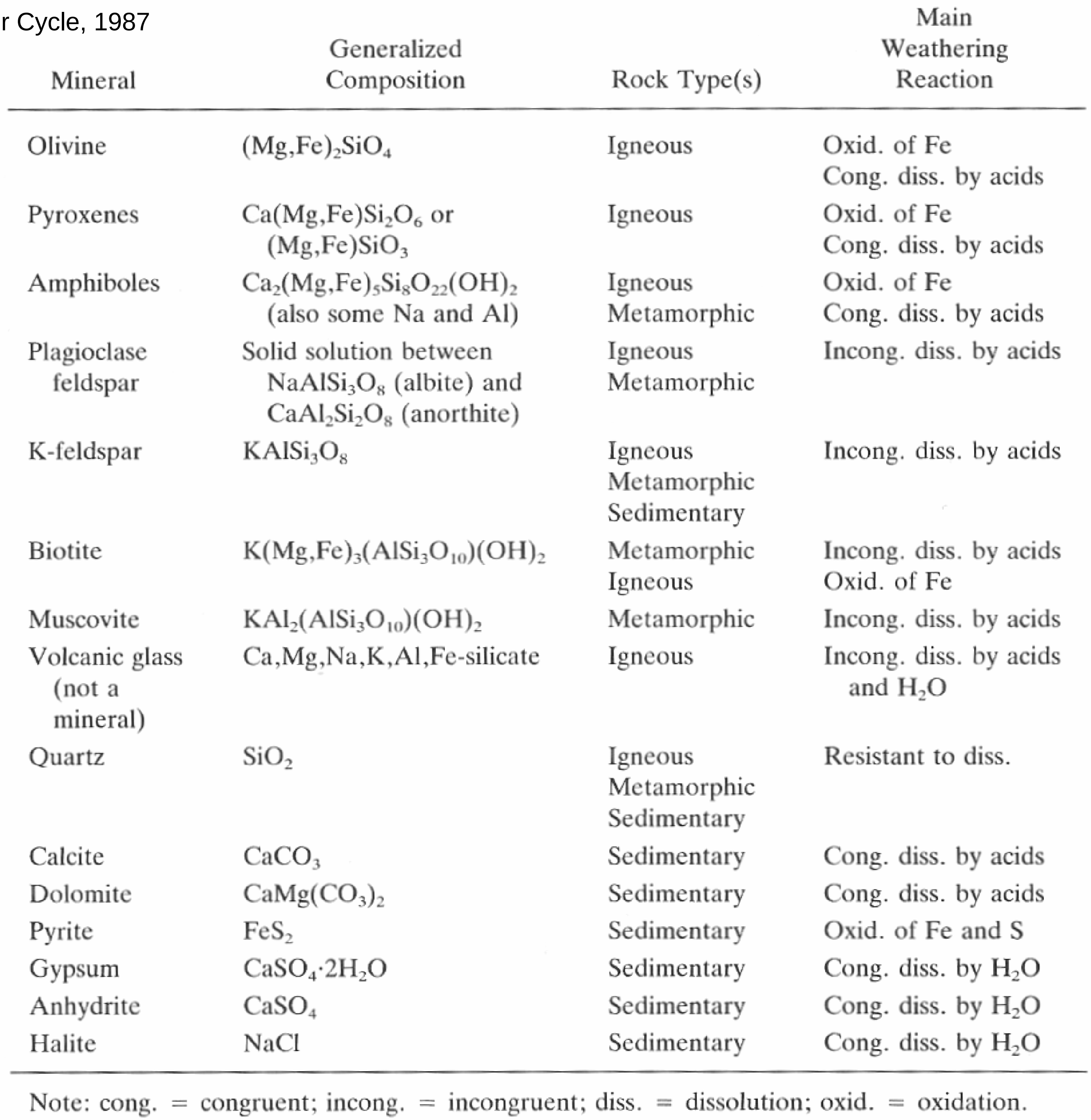
- Double chains: Amphiboles
  - Two planes @ 60° & 120°



http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld039.htm

Table 4.3 Berner, The Global Water Cycle, 1987

Common Primary Minerals that Undergo Weathering

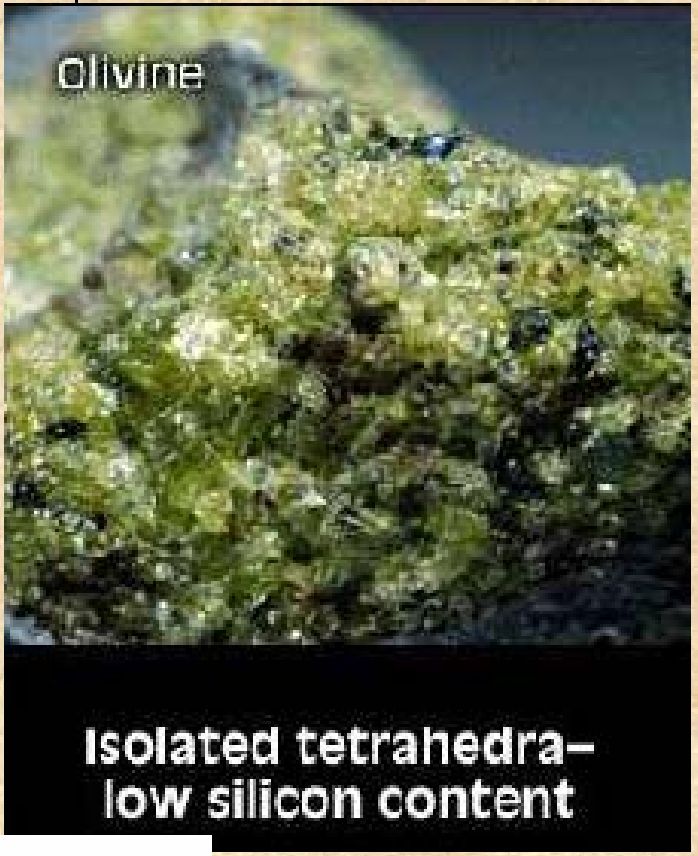


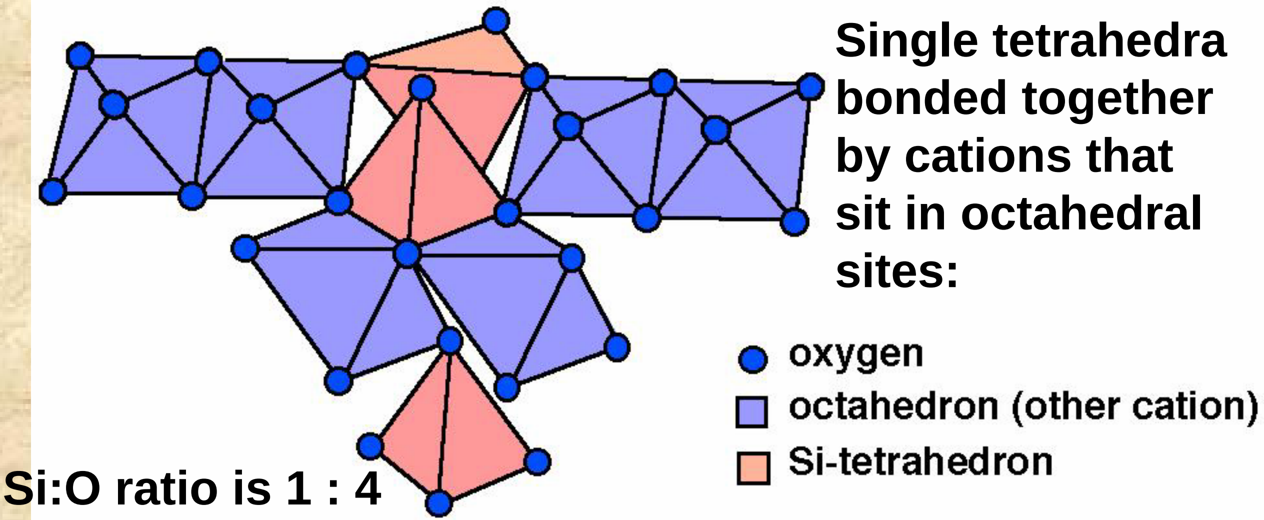
Mineral	Generalized Composition	Rock Type(s)	Main Weathering Reaction
Olivine	$(Mg,Fe)_2SiO_4$	Igneous	Oxid. of Fe Cong. diss. by acids
Pyroxenes	$Ca(Mg,Fe)Si_2O_6$ or $(Mg,Fe)SiO_3$	Igneous	Oxid. of Fe Cong. diss. by acids
Amphiboles	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ (also some Na and Al)	Igneous Metamorphic	Oxid. of Fe Cong. diss. by acids
Plagioclase feldspar	Solid solution between $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (anorthite)	Igneous Metamorphic	Incong. diss. by acids
K-feldspar	$KAlSi_3O_8$	Igneous Metamorphic Sedimentary	Incong. diss. by acids
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Metamorphic Igneous	Incong. diss. by acids Oxid. of Fe
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Metamorphic	Incong. diss. by acids
Volcanic glass (not a mineral)	Ca,Mg,Na,K,Al,Fe-silicate	Igneous	Incong. diss. by acids and H_2O
Quartz	SiO_2	Igneous Metamorphic Sedimentary	Resistant to diss.
Calcite	$CaCO_3$	Sedimentary	Cong. diss. by acids
Dolomite	$CaMg(CO_3)_2$	Sedimentary	Cong. diss. by acids
Pyrite	FeS_2	Sedimentary	Oxid. of Fe and S
Gypsum	$CaSO_4 \cdot 2H_2O$	Sedimentary	Cong. diss. by H_2O
Anhydrite	$CaSO_4$	Sedimentary	Cong. diss. by H_2O
Halite	NaCl	Sedimentary	Cong. diss. by H_2O

Note: cong. = congruent; incong. = incongruent; diss. = dissolution; oxid. = oxidation.

- Olivine: forms at highest temperatures and is most readily broken down at the surface of the earth (This is because it is the most OUT of equilibrium with the conditions that exist at the surface of the earth.) Has either Fe or Mg holding together the tetrahedra.

http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld041.htm



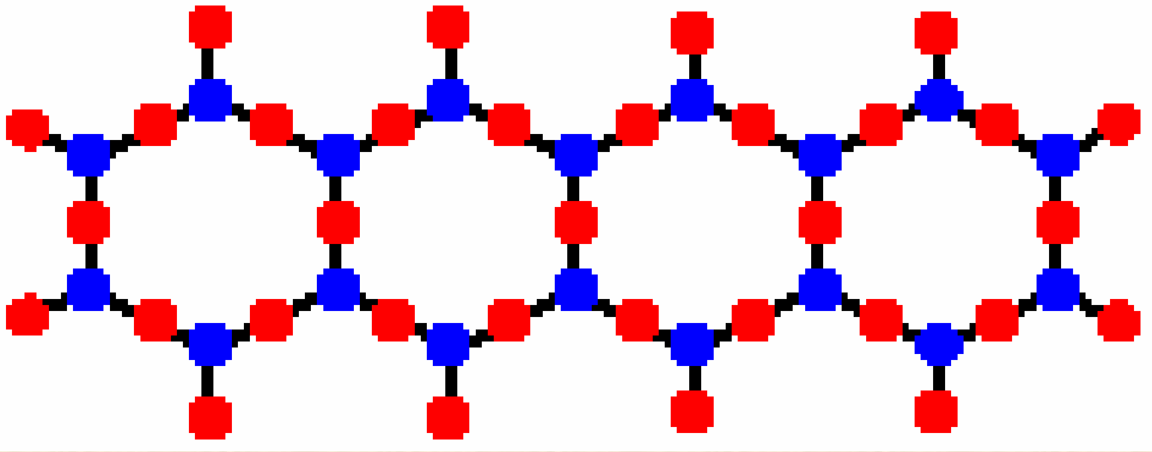


Single tetrahedra bonded together by cations that sit in octahedral sites:

Si:O ratio is 1 : 4

http://classes.colgate.edu/rapril/geol201/summaries/silicates/neso.htm

- Amphiboles and Biotite contain water in their structure.
- Pyroxenes: silicate chains. SiO_3 not SiO_4 because 1 oxygen is shared along the chain, each Mg will share an oxygen.

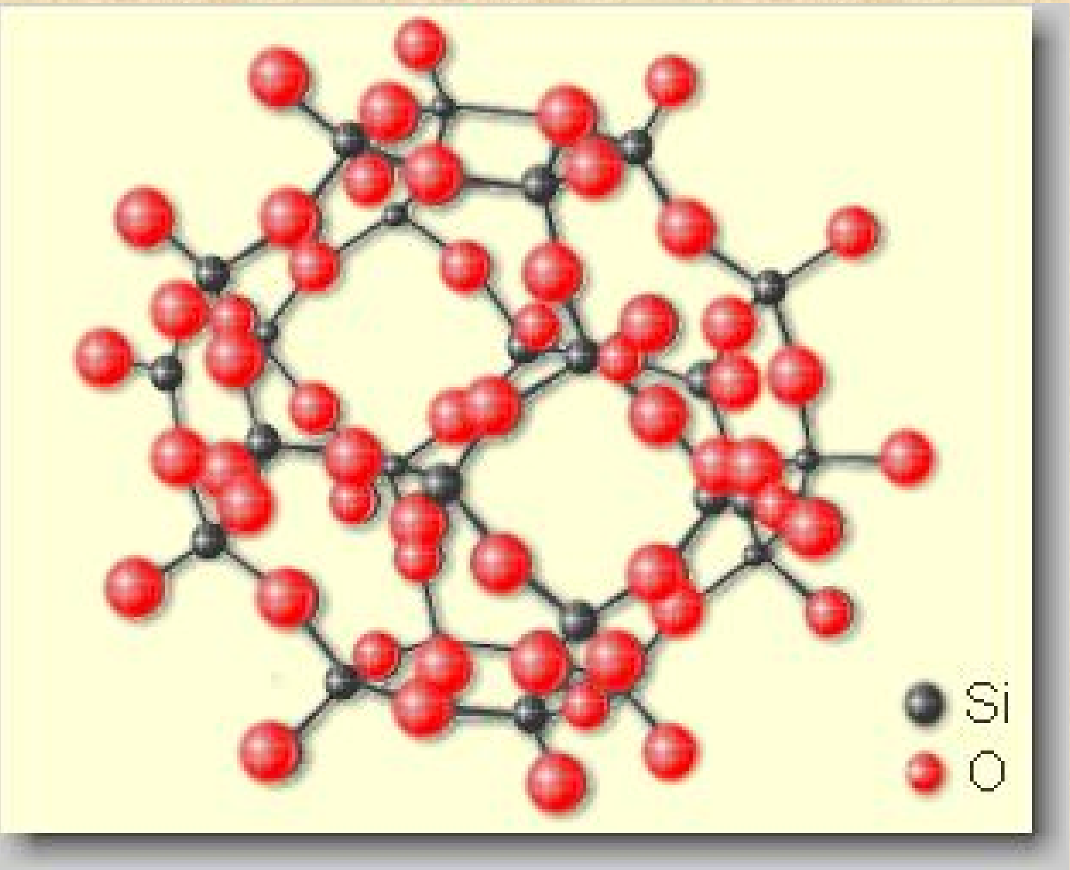


http://www.brookes.ac.uk/geology/sem/EDS/edsspec1.html

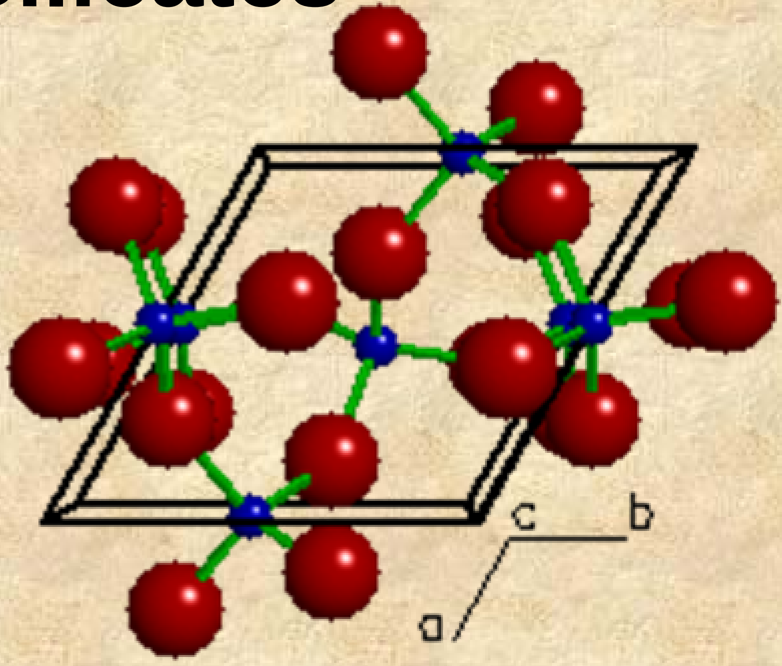
- Those that form at high temperatures are much less in equilibrium with conditions at the surface of the earth- the desire of the system to produce equilibrium.
- Those with water in their structure are the most stable.
- Muscovite is more resistant than biotite.

http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

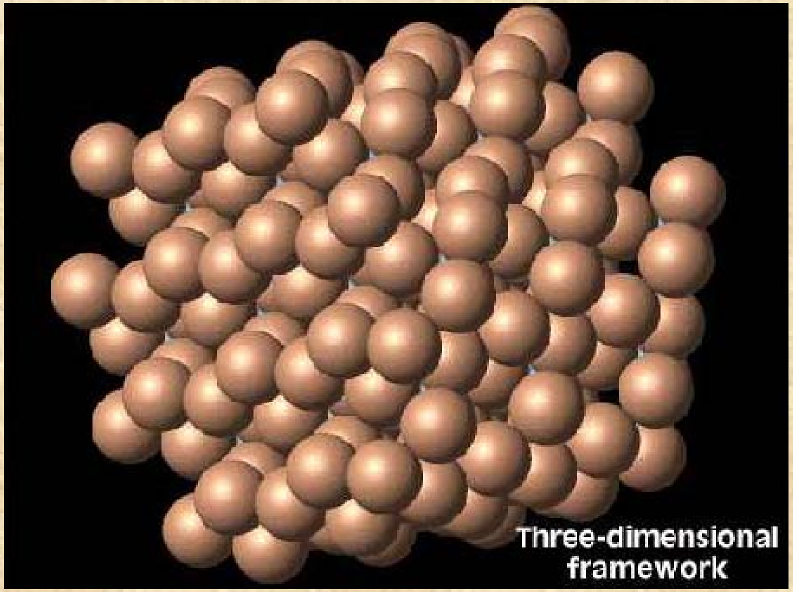
Framework Silicates



http://www.a-m.de/englisch/lexikon/mineral/silicate.htm



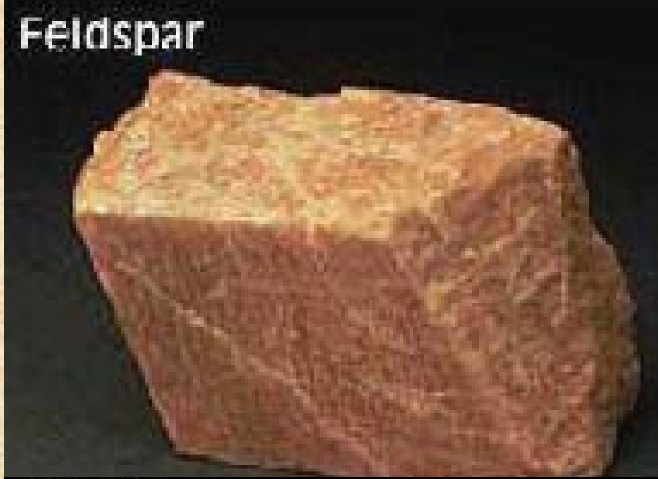
http://www.science.uwaterloo.ca/~cchieh/cact/applychem/silicate.html



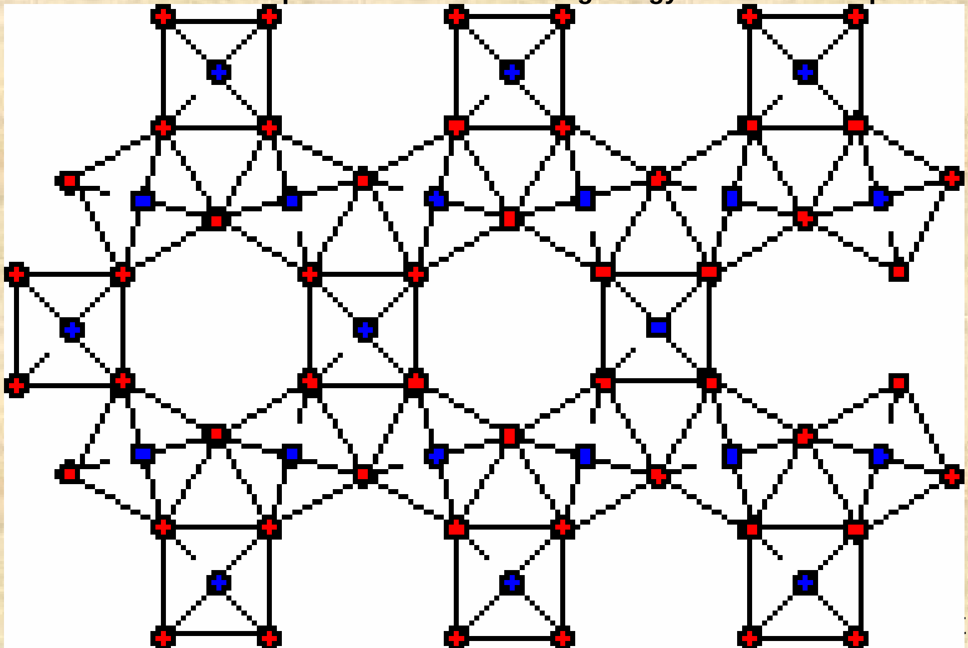
http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

- K-feldspar, Quartz and Muscovite are all framework silicates- framework of O with the silica in the center of the tetrahedra- all of the oxygens are being shared (therefore SiO_2 as opposed to SiO_4 due to the sharing of the oxygens, etc).

  → They are very resistant to weathering- Much more stable at earth's surface than the mafics. Quartz appears in sand (e.g. at beach etc).



http://www.brookes.ac.uk/geology/sem/EDS/edsspec1.html



p://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

Mineral Weatherability
(Decreasing from top-to-bottom

- Halite Least resistant to weathering
- Gypsum-anhydrite
- Pyrite
- Calcite
- Dolomite
- Volcanic glass
- Olivine
- Ca-plagioclase
- Pyroxines
- Ca-Na plagioclase
- Amphiboles
- Biotite
- K-feldspar
- Muscovite
- Vermiculite, smectite
- Quartz
- Kaolinite
- Gibbsite, hematite, geothite

Most resistant to weathering

http://resourcescommittee.house.gov/subcommittees/emr/usgsweb/photogallery/

Note: Minerals are listed in order of increasing resistance to weathering. (Exact positions for some minerals can change one or two places due to effects of grain size, climate, etc.)

Table 4.5 Berner, The Global Water Cycle, 1987

Fe^{2+} (ferrous) present in igneous rock. In the presence of O_2, it oxidizes to Fe^{3+}.

$$Fe^{2+} \rightarrow Fe^{3+} \rightarrow FeO(OH)$$

•This reactions occurs almost immediately- no stability whatsoever. However, Fe^{3+} is essentially totally insoluble in water and forms FeOOH. Forms oxides and hydroxides (i.e. rust, iron staining- hard to wash away)

http://www.emdesigns.com/findus/hmb/rocks/rust_rock-big.jpg

** For our purposes we are worried about the base cations, especially Mg and Ca.

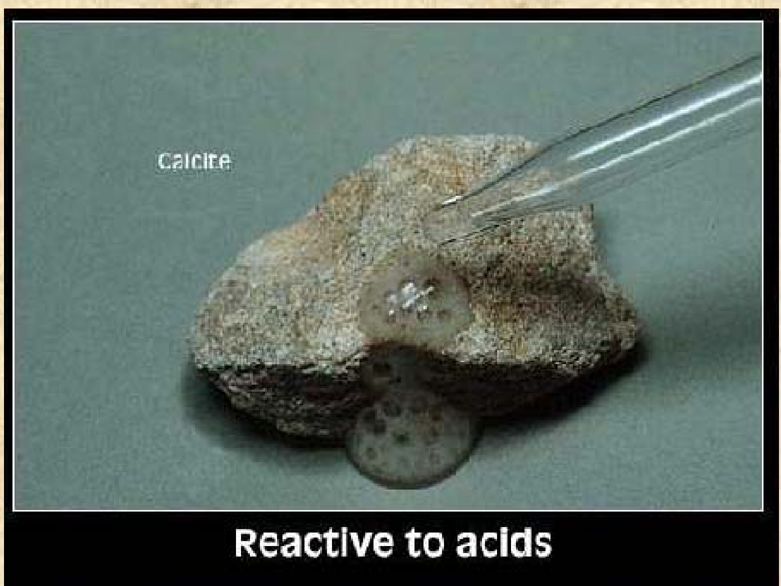
Restore Equilibrium via Weathering

- must first get activation energy to start processes.
- Water greatly accelerates this process.

(i.e. On the moon, rocks that are 4.4 Billion years old are fresher than the youngest rocks on earth- because the moon has no water).

* 3 Process that Occur:

1) *Hydration*: weathering products are hydrated
2) *Cation Loss:* cation removed from high- temp. product & the ratio of cation to Si + A drops.
3) *Neutralize acid*: Natural acids are agents of weathering which in turn results in neutralizing that acid (Trees do generate acids which accelerate the weathering process).



http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

** Exchange of H^+ in water ←→ Cation

* Weathering of plagioclase:

$\mathbf{CaAl_2Si_2O_8}$ + H_2O + $2H^+$ → Ca^{++} (goes into water) + $\mathbf{Al_2Si_2O_5(OH)_4}$

(Plagioclase) **(Kaolinite)**

- Kaolinite : typical clay structure, a low-temperature mineral that is most stable at the condition of the earth's surface;   the end product of weathering.

➔ Removing cations, adding OH, neutralizes acids.

http://resourcescommittee.house.gov/subcommittees/emr/usgsweb/photogallery/

Figure 4.5 Berner, The Global Water Cycle, 1987

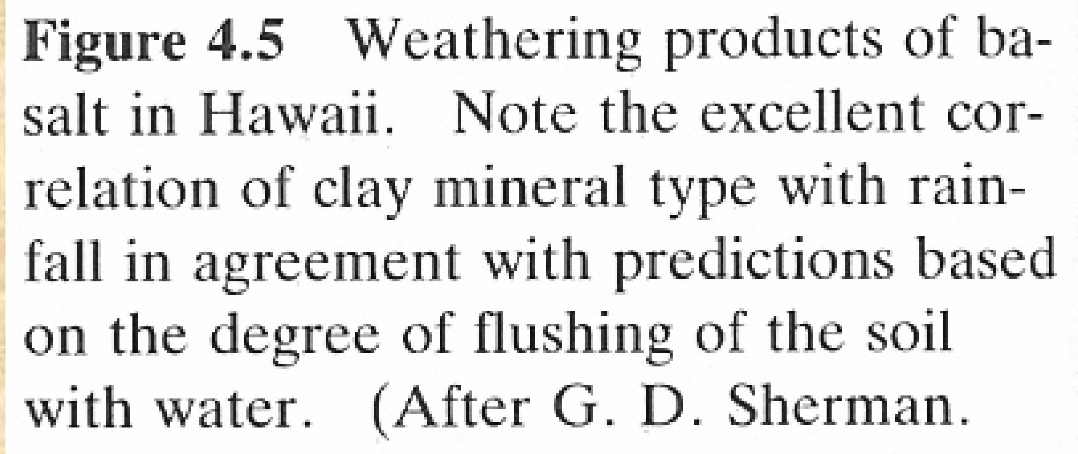
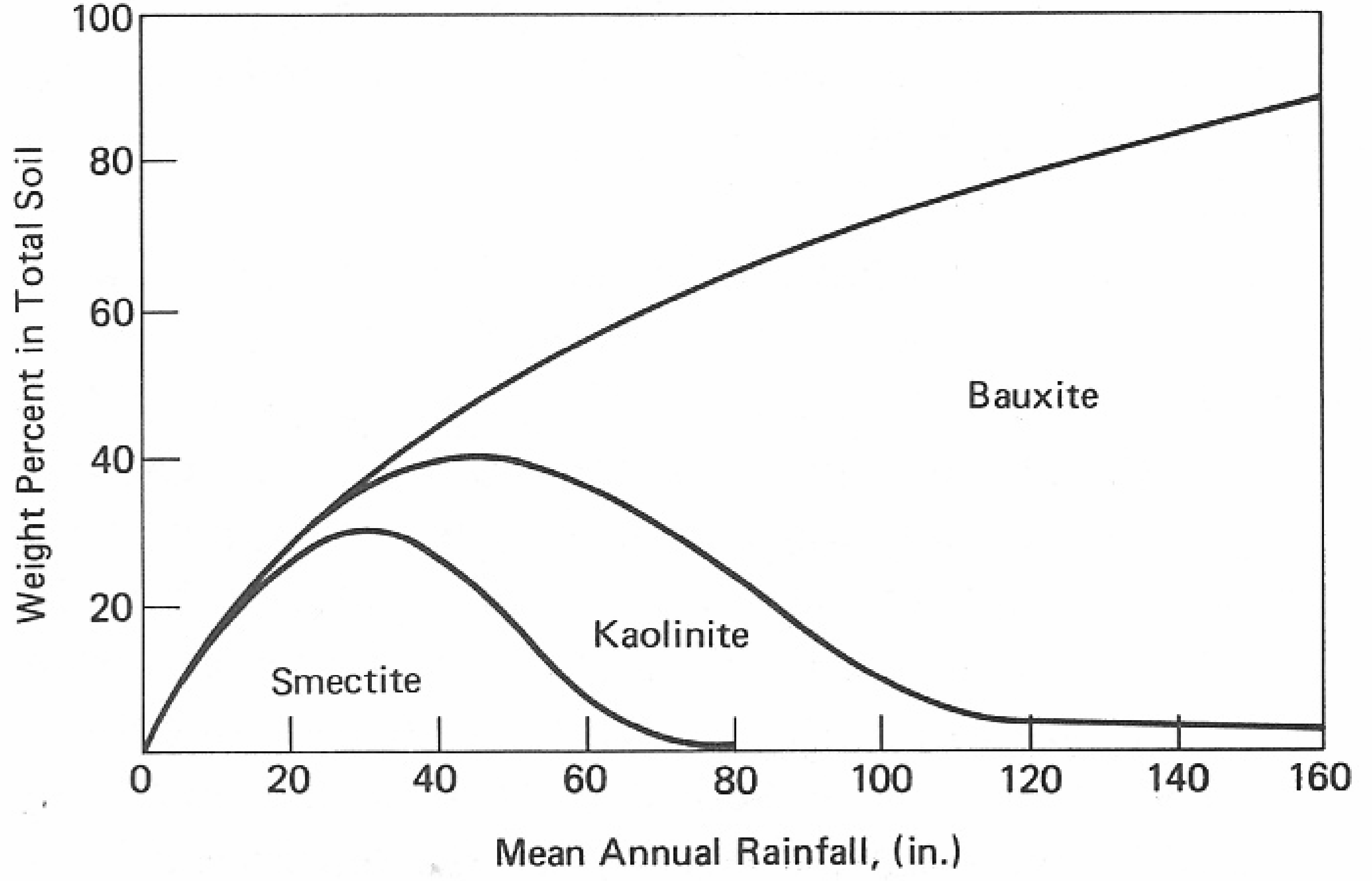


Figure 4.5 Weathering products of basalt in Hawaii. Note the excellent correlation of clay mineral type with rainfall in agreement with predictions based on the degree of flushing of the soil with water. (After G. D. Sherman.



Carbonate Weathering

- large amounts of calcite is the reason, in general, why places such as Rochester and the Mid-Eastern states don't have problems with acid rain.
- Problem of acid rain: Determined basically by the presence of absence of calcite- Tells how sensitive an area will be to acid.

Calcite reacting to acid

Simplified reactions (removes H^+ ions)

$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{++} + 2HCO_3^-$ → pH ~ 7 - 7.5 of bicarbonate; water with about neutral

(Calcite) (Carbonic acid) (bicarbonate)

↑ ↑ ↑

http://lewis.up.edu/mcs/wasowski/sci110/TnTkCh02/sld001.htm

Concentration of calcium in equilibrium with calcite as a function of P_{C0_2} in the system of $CaCO_3$-CO_2-H_20 at 25°C and 1 atm total pressure.

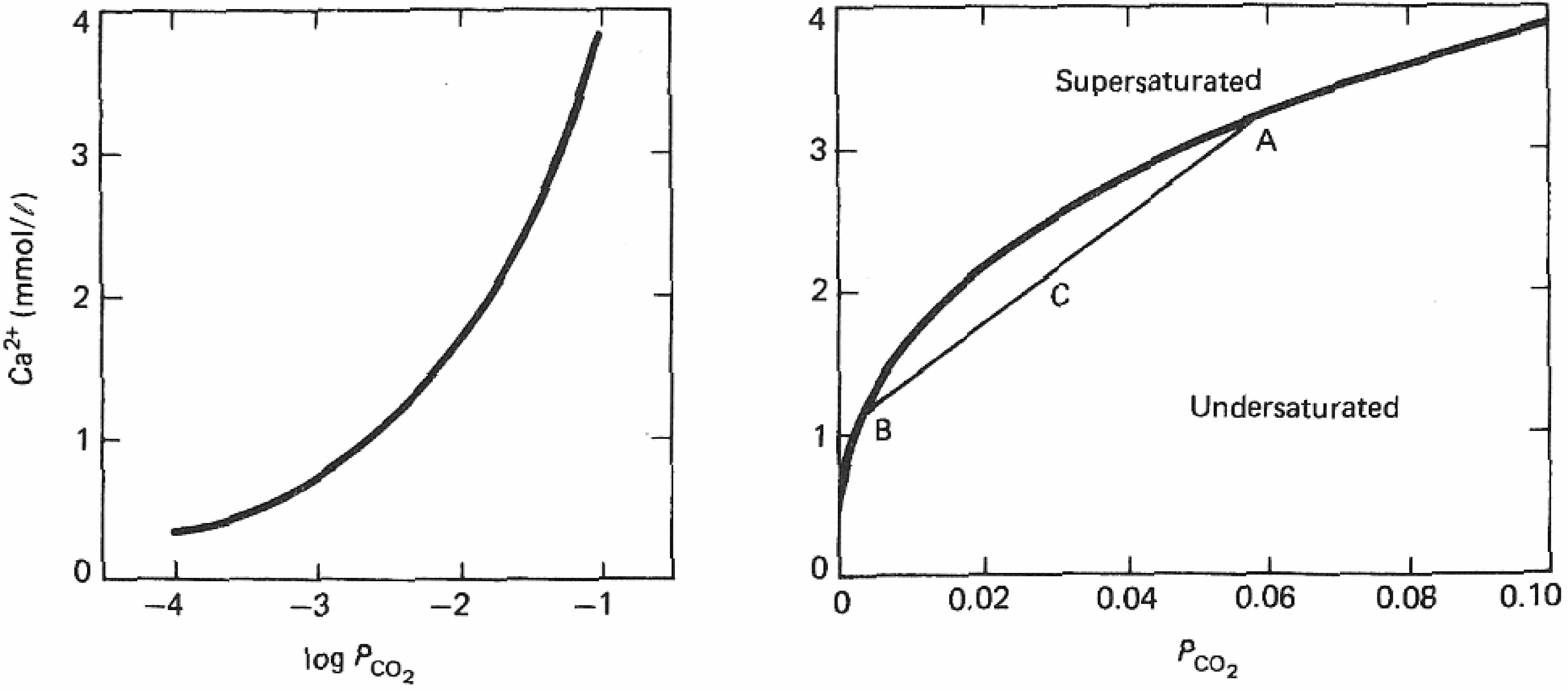
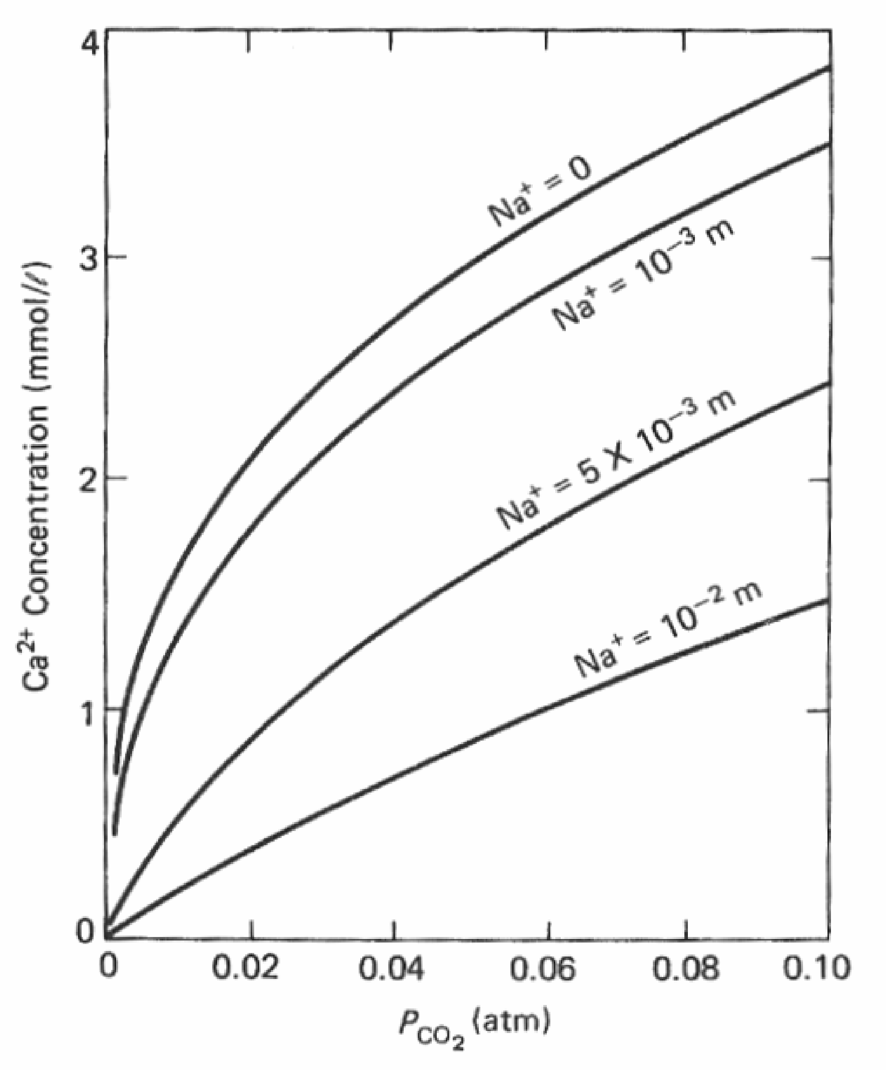


Figure 3-4. Drever, *The Geochemistry of Natural Water*

Concentration of calcium in equilibrium with calcite as a function P_{C0_2} and Na^+ concentration in the system of $CaCO_3$- Na_2CO_3-CO_2-H_20 at 25°C and 1 atm total pressure.



Concentration of calcium in equilibrium with calcite as a function P_{C0_2} and Cl^- concentration in the system of $CaCO_3$- $CaCl_2$-CO_2-H_20 at 25°C and 1 atm total pressure.

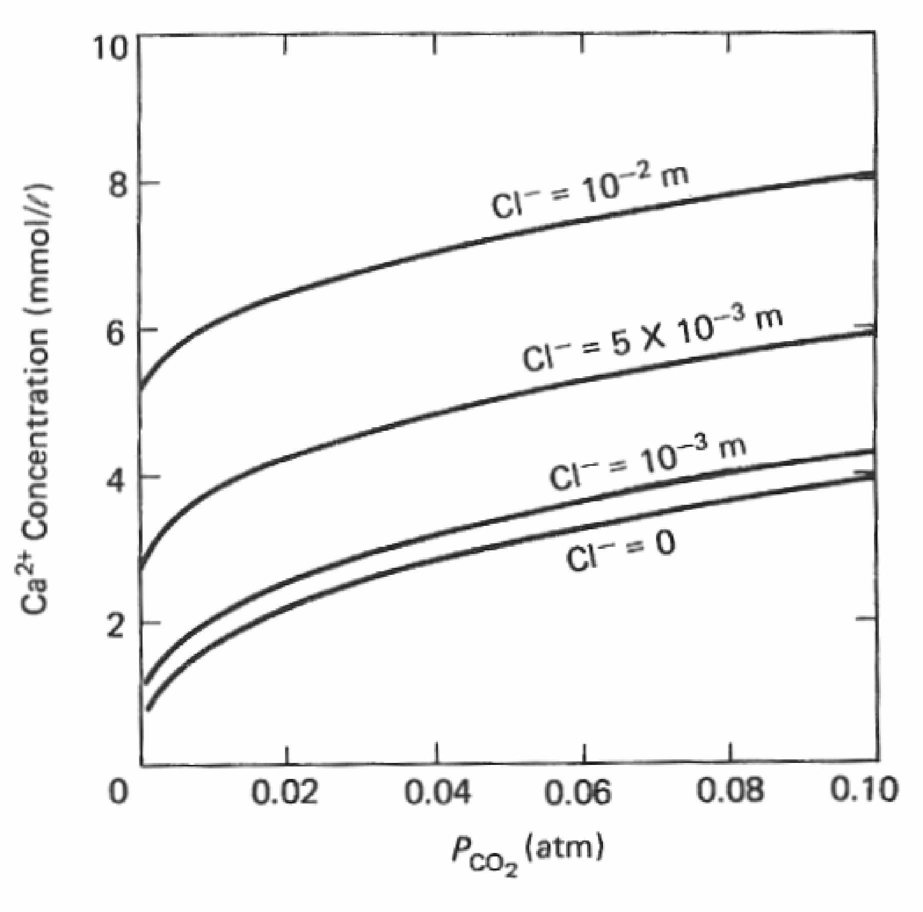


Figure 3-5,6. Drever, *The Geochemistry of Natural Waters*

Changes in composition of carbonated water as it equilibrates with calcite when the system is either open or closed to exchange of CO2 gas. Initial P_{C0_2} values of 10^{-2} and 10^{-1} atm.

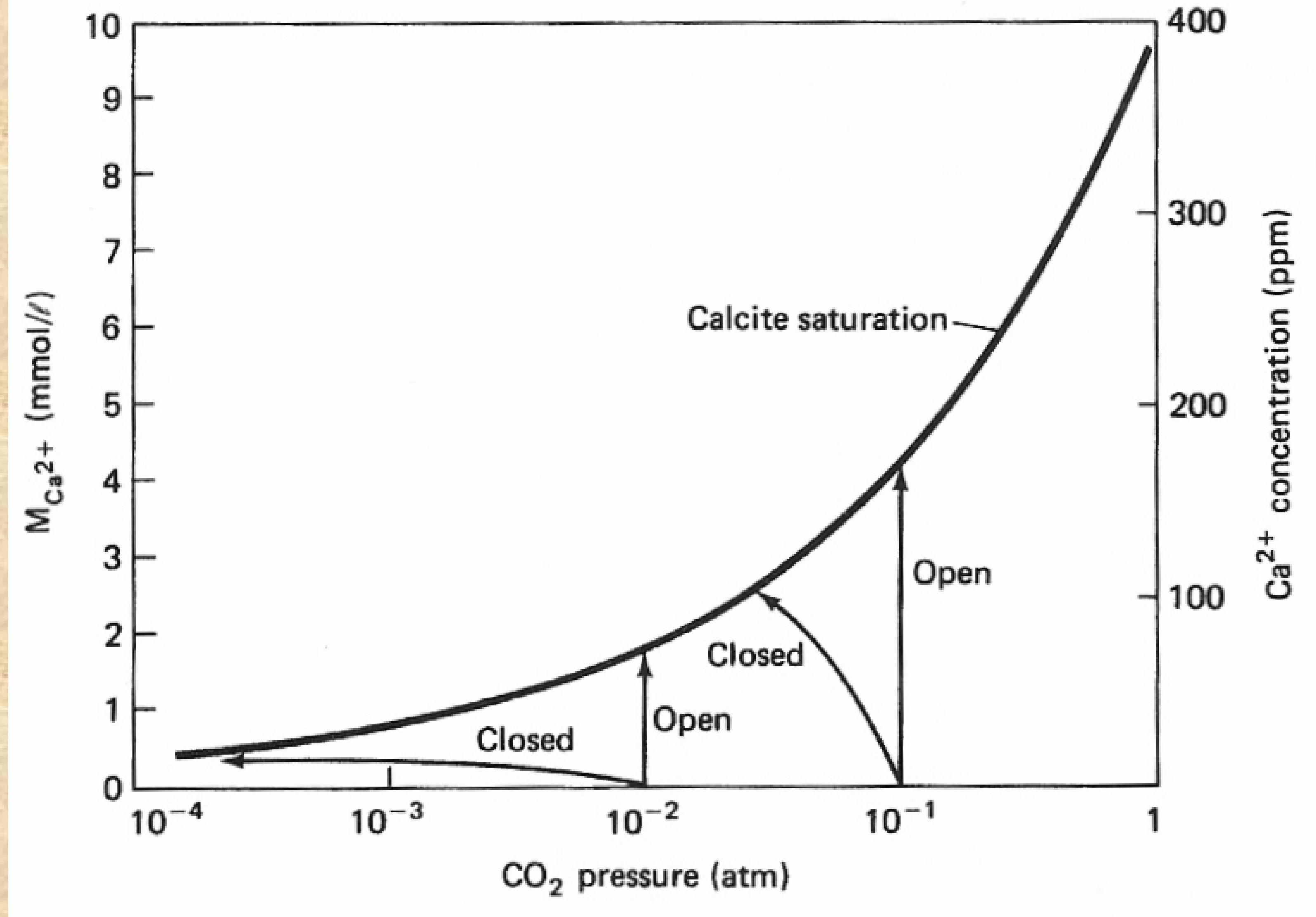


Figure 3-8. Drever, *The Geochemistry of Natural Waters*

* Reactions are quite congruent, structure not attacked; simple reactions.

* Acid Precipitation:

$2CaCO_3 + 2H^+ + SO_4^= \rightarrow 2Ca^{++} + SO_4^= + 2HCO_3^-$

* There are natural acids

ie. In rain CO_2 in the atmosphere (pH = 5.6)

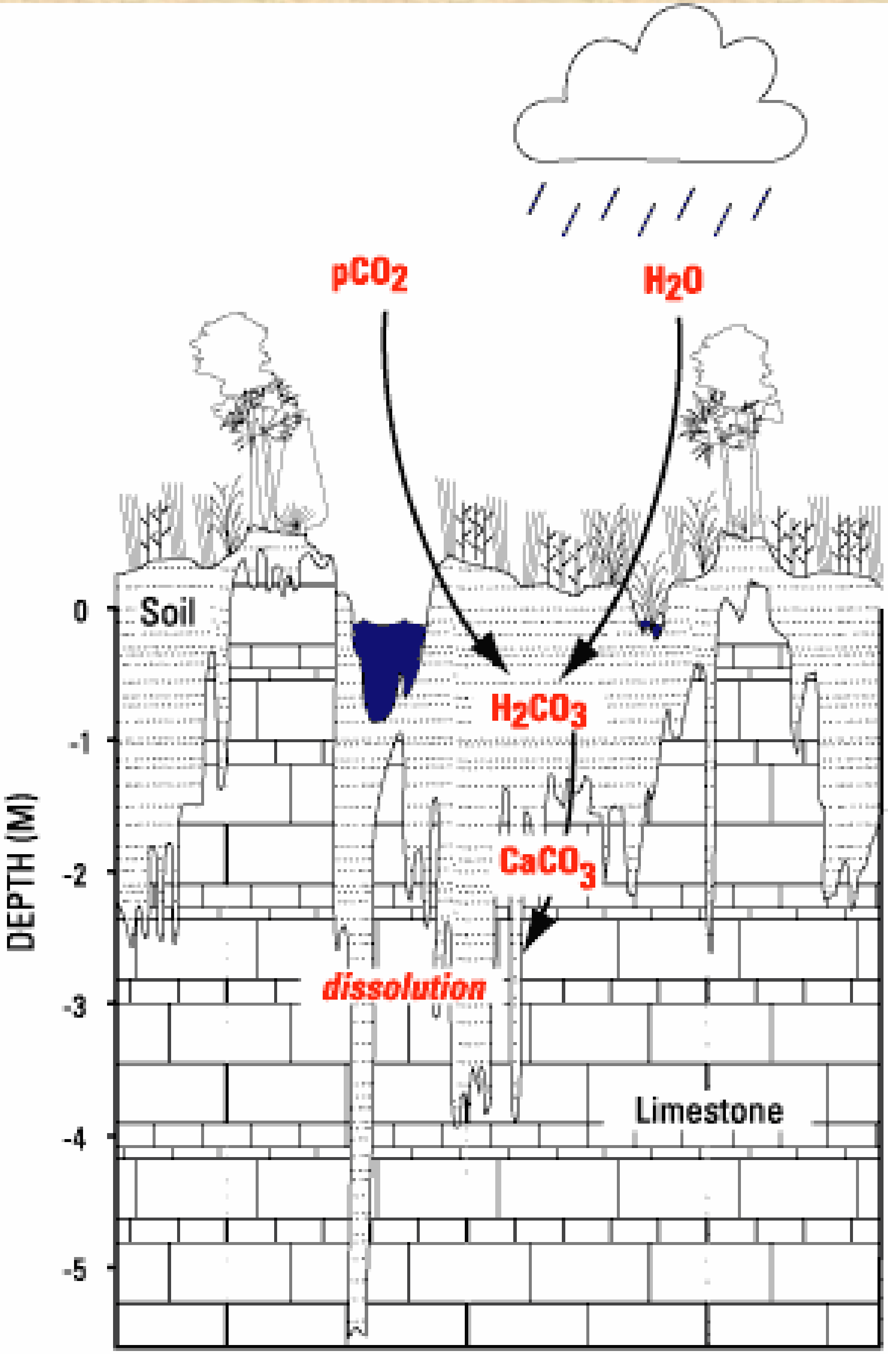
$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO^{3-}$

PCO_2 ~ 350 ppm → pH = 5.6

* Rate of carbonate weathering is about 100 times the rate of silicate weathering.

- ie. Florida- formation of karst due to the dissolving of calcite- wouldn't see that with silica.

Florida karst formation



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

- Bacterial and root respiration in the soil increase pCO_2
- As pCO_2 increases, so do dissolution rates

Tropical latitudes = high evapotranspiration
+ well developed soil
+ high atm. pCO_2
= KARST

(Yucatan, Caribbean, Florida, South China...)

http://coastal.er.usgs.gov/publications/ofr/00-180/intro/fig9.html

Solution and collapse features of karst and karren topography

http://coastal.er.usgs.gov/publications/ofr/00-180/intro/karst.html

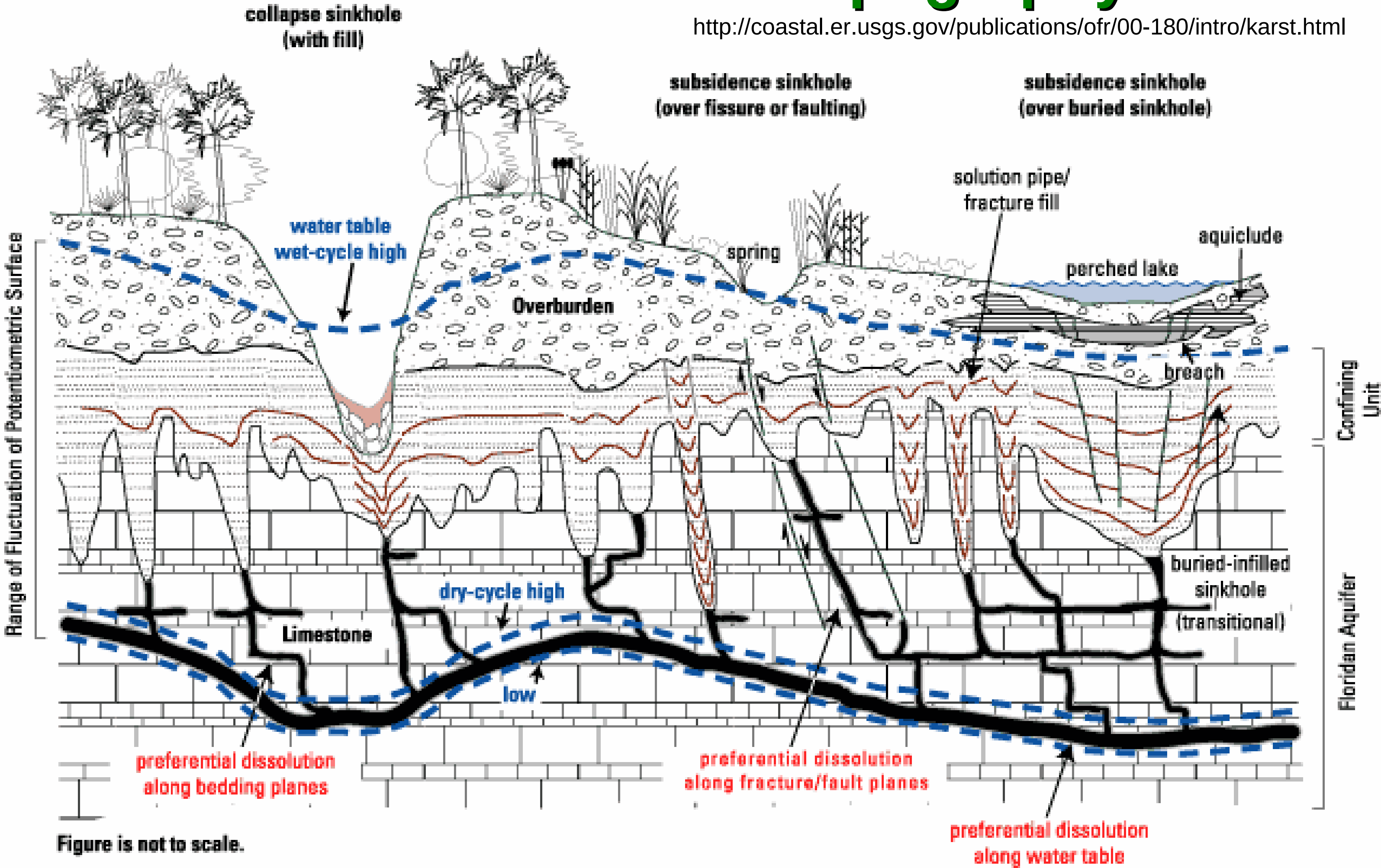


Figure is not to scale.

Distribution of major species of dissolved inorganic carbon at 20°C

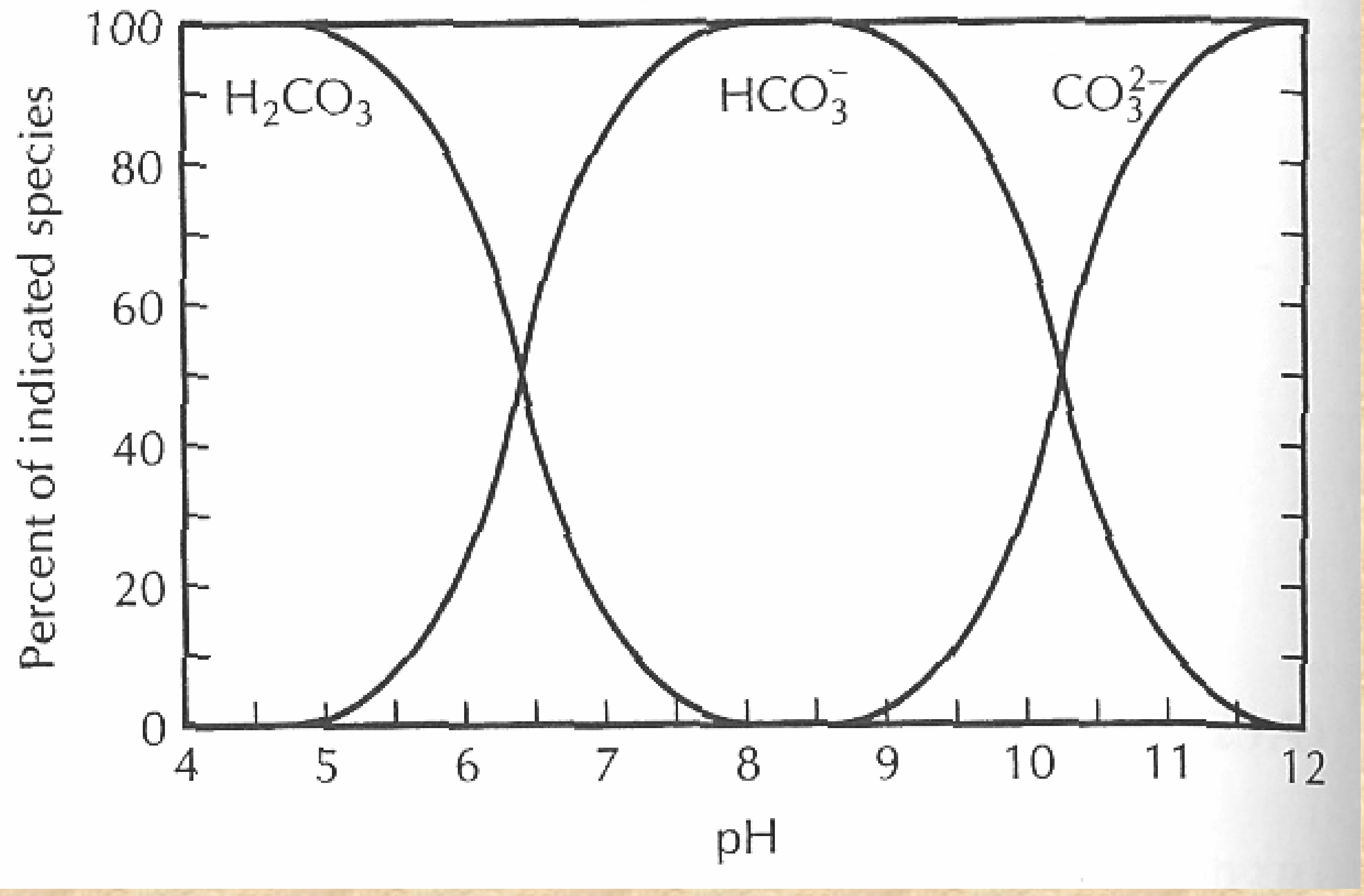
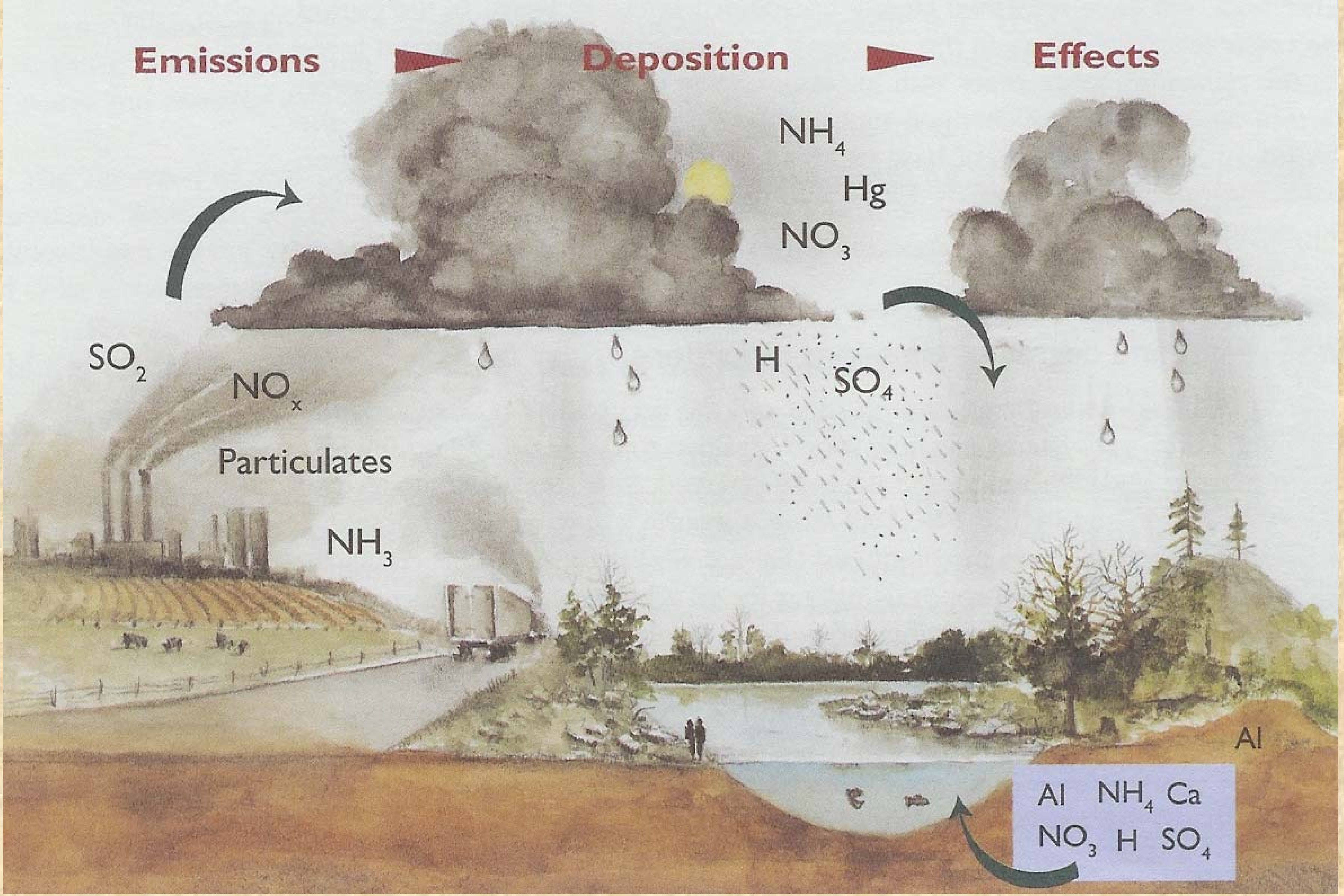


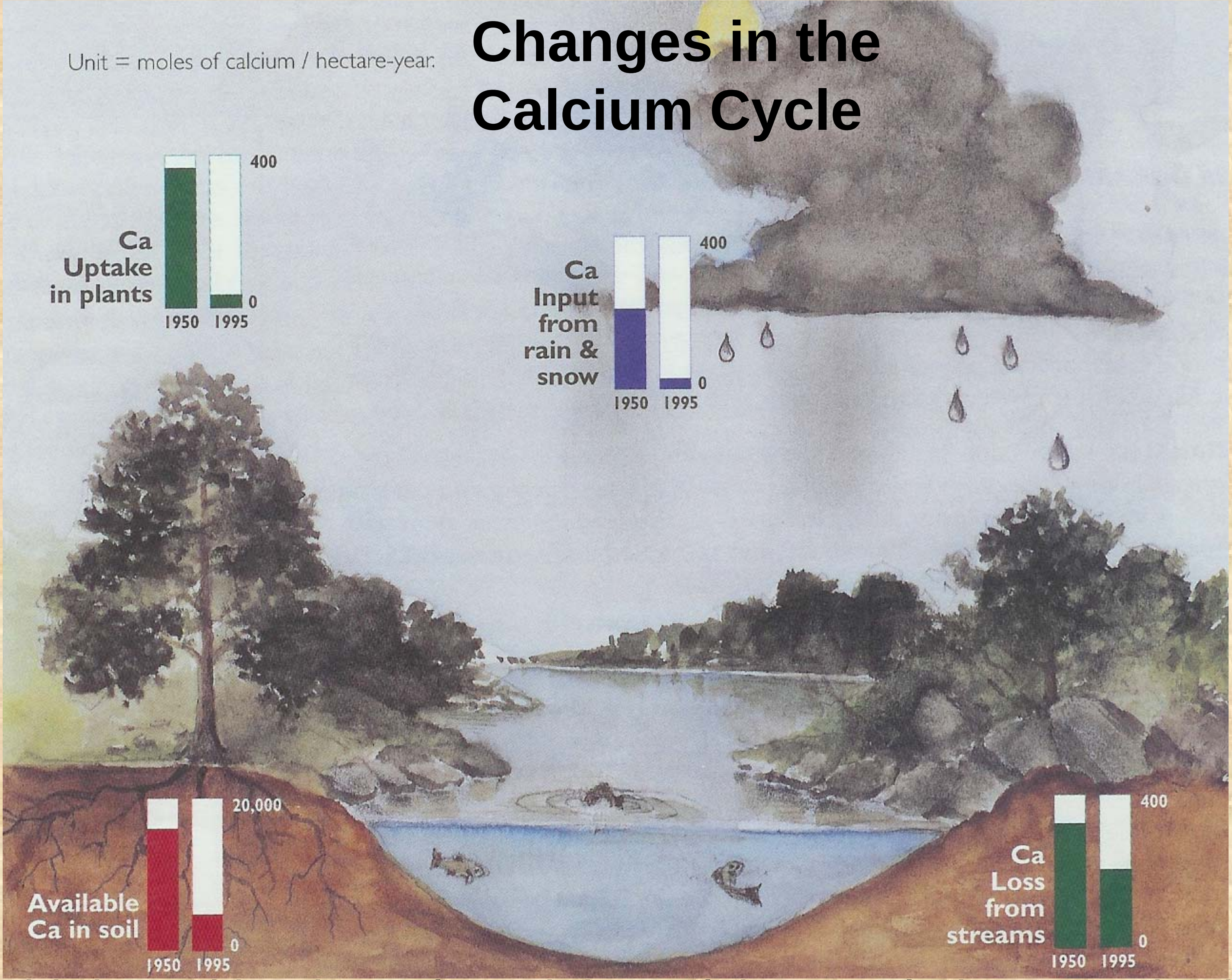
Figure 9.1 Fetter, *Applied Hydrogeology 4th Edition*



Acid deposition is a complex problem that originates with the burning of fossil fuels and leads to the deposition of acids, setting off a series of ecological effects.

Figure 1. “Acid Rain Revisited.” HBRF

Changes in the Calcium Cycle



Acid deposition has altered the calcium cycle in watersheds in the Northeast that are similar to the HBEF.

Figure 8. “Acid Rain Revisited.” HBRF

Organic acids (e.g.. Oxalic acid)

* Organic material breaks down and releases acids (pH ~ 5). These natural acids play an important role in weathering in absence of human activity; behaves very much like carbonic acid

$$4H_2C_2O_4 \text{ (oxalic acid)} + 2O_2 \rightarrow \underset{\underset{H_2CO_3^{--}}{\uparrow}}{8CO_2} + 4H_2O$$

The Mass- Balance Approach

Trees produce acid. This represents the typical soil with tree → with the soil horizons dependent upon soil productivity. (12,000 year)

Soil Horizons

O horizon ---> Organic acids (large organic molecules)-
Humic Fulvic, pH<5 ; 10 cm - 1 m

Kaolinite (tropical)
Illite (temperate)
Bauxite (Aluminum hydroxide, tropical)

A horizon ---> zone of leaching
Al, Si, OH. Stripped of all Mg, K, Ca and Na bearing minerals

B horizon ---> zone of accumulation
Clays ---> Pool of exchangeable cations
Fe, Al Hydroxides, Clays
Ca^{++}, Mg^{++}, K^{+}, Na^{+} (Base Cations)

C horizon ---> partly decomposed
unaltered bedrock
weathering

- A horizon - size of zone can change: deciduous or temperate: about 1 meter; tropical: about 5 - 10 meters. Organic acids have a lot of H+ for weathering.
- B horizon: Where the tree extends root system into:
  - Clays, weathered mineral material
  - Clay hydroxides with Ca, Mg, K, N have attached (Ca, Mg, and K are exchangeable cations because clays have charged surfaces and attract cations)
- C horizon: Partially decomposed and unaltered bedrock

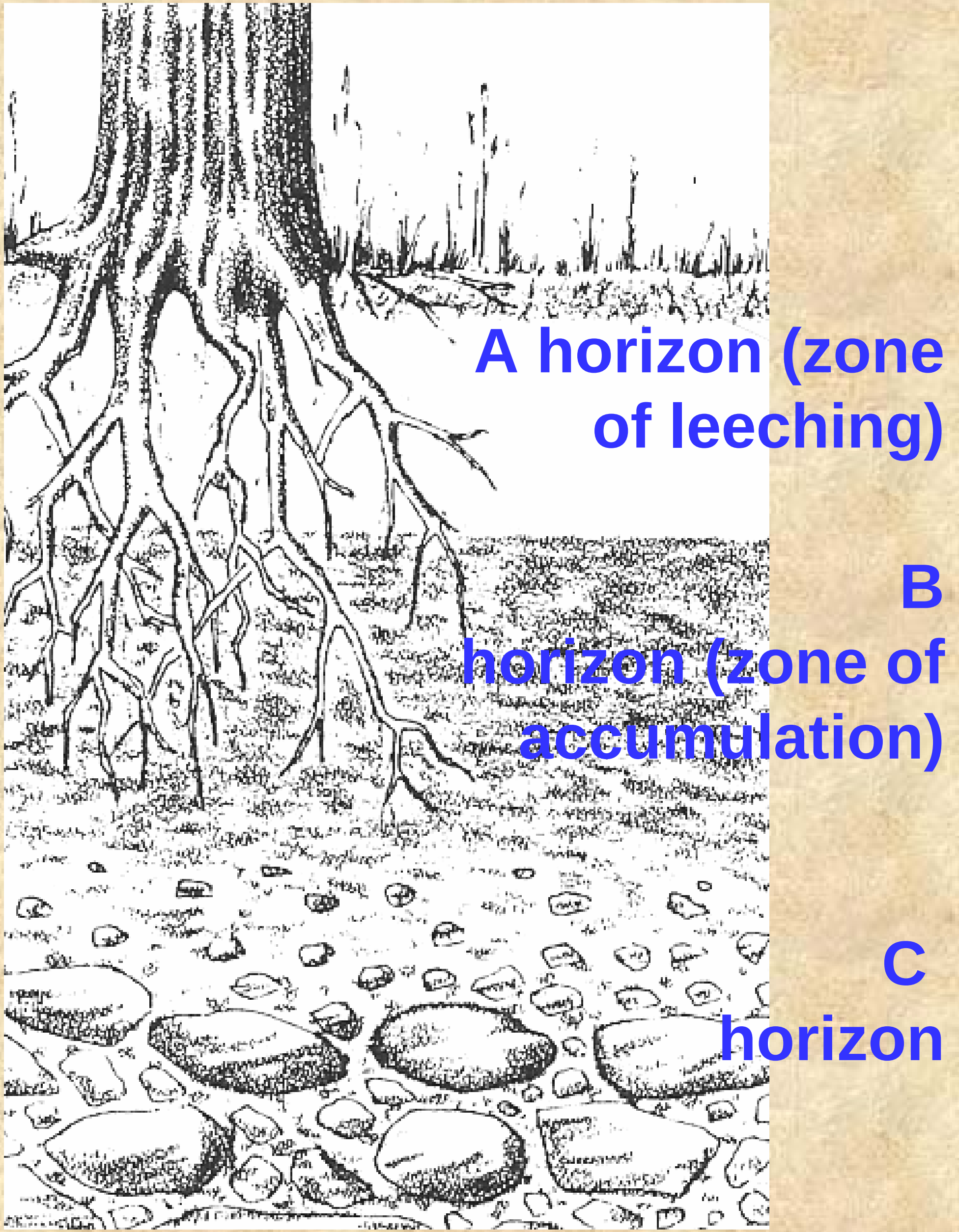
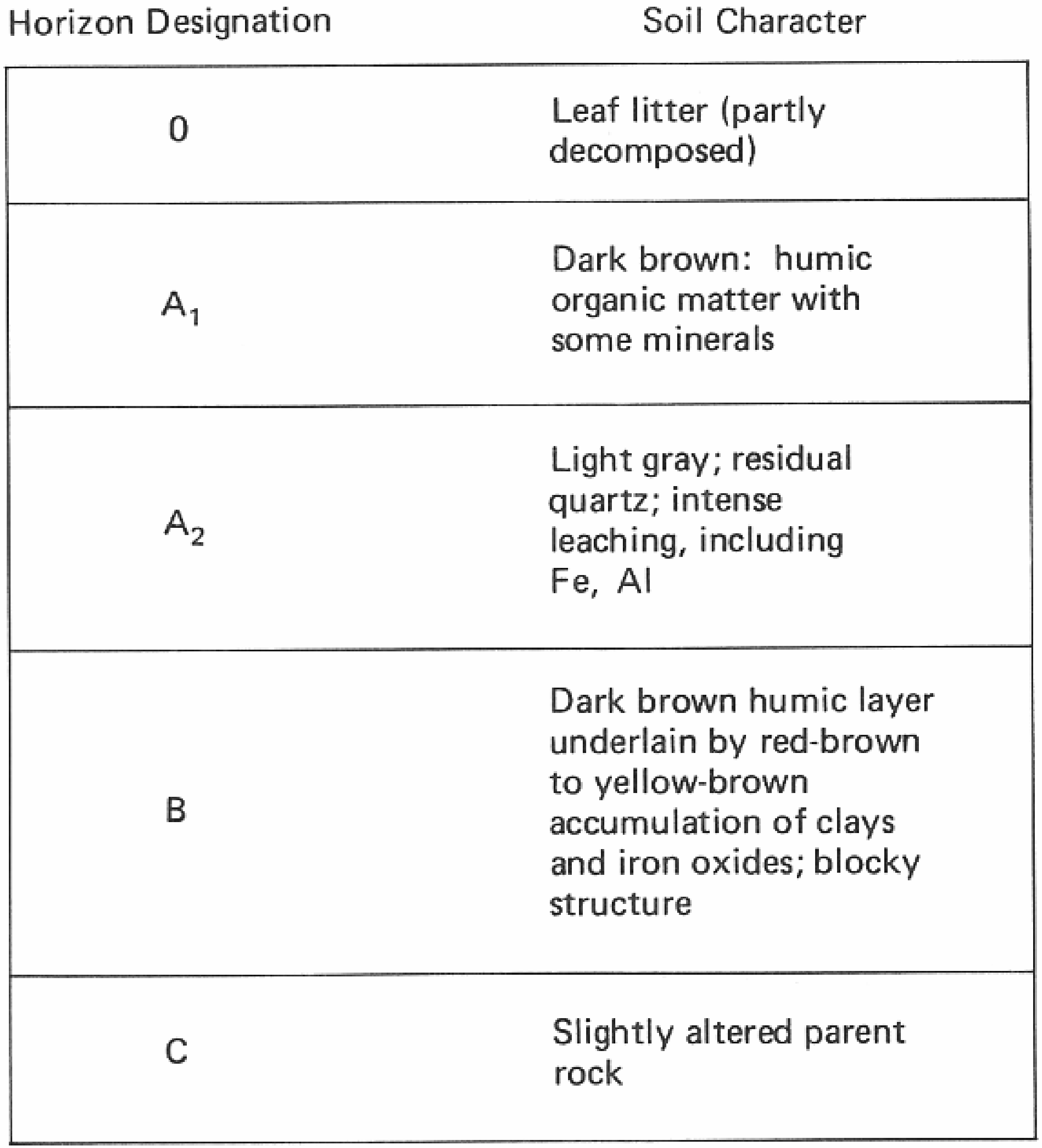


Figure 12-1 Drever, *The Geochemistry of Natural Waters*, 1997

Simplified vertical profile of a typical podzolic soil of a humid temperate climate



Horizon Designation	Soil Character
0	Leaf litter (partly decomposed)
A_1	Dark brown: humic organic matter with some minerals
A_2	Light gray; residual quartz; intense leaching, including Fe, Al
B	Dark brown humic layer underlain by red-brown to yellow-brown accumulation of clays and iron oxides; blocky structure
C	Slightly altered parent rock

Figure 4.7. Berner. *The Global Water Cycle*, 1987.

Cation weathering rates:

Highest → Ca, Mg, Na

→ K, Si

Least → Fe, Al (under normal conditions, Fe remains as clay, hydroxides)

* Trees are crucial in the weathering process.

Biology (e.g. Trees)

800 CO_2 + 6NH^{4+} + 4Ca^{2+} + Mg $^{2+}$ + 2K+ + 1$Al(OH)^{2+}$ + Fe^{2+} + 2NO^{3-} + $H_2PO_4^-$ + $SO_4^=$ → 804O_2 + Biomass + 16H^+

* Must excrete H^+ for charge balance.

* Removes cations → supplied by decomposition

- Logging → Permanent removal
- Fire → returns cations; releases anions to atmosphere; releases mostly NO_x. Slash and burn process essential to tropics because so much of the cations are stored in the biomass.

http://www.srs.fs.usda.gov/gallery/management_activities.htm

http://www.elephants.com/a_slash.htm

Base Cation Transport

- Acid rain picks up Base+ from leaves
- Neutralized; extracts Base+ from soil

  "mines" cations from soil → H^+

- Direct acid effects → acid fog, mist can have a pH of 2.

http://www.eco-systems.org/acidfog_in_CA.htm

ACID DEPOSITION EFFECTS ON TREES

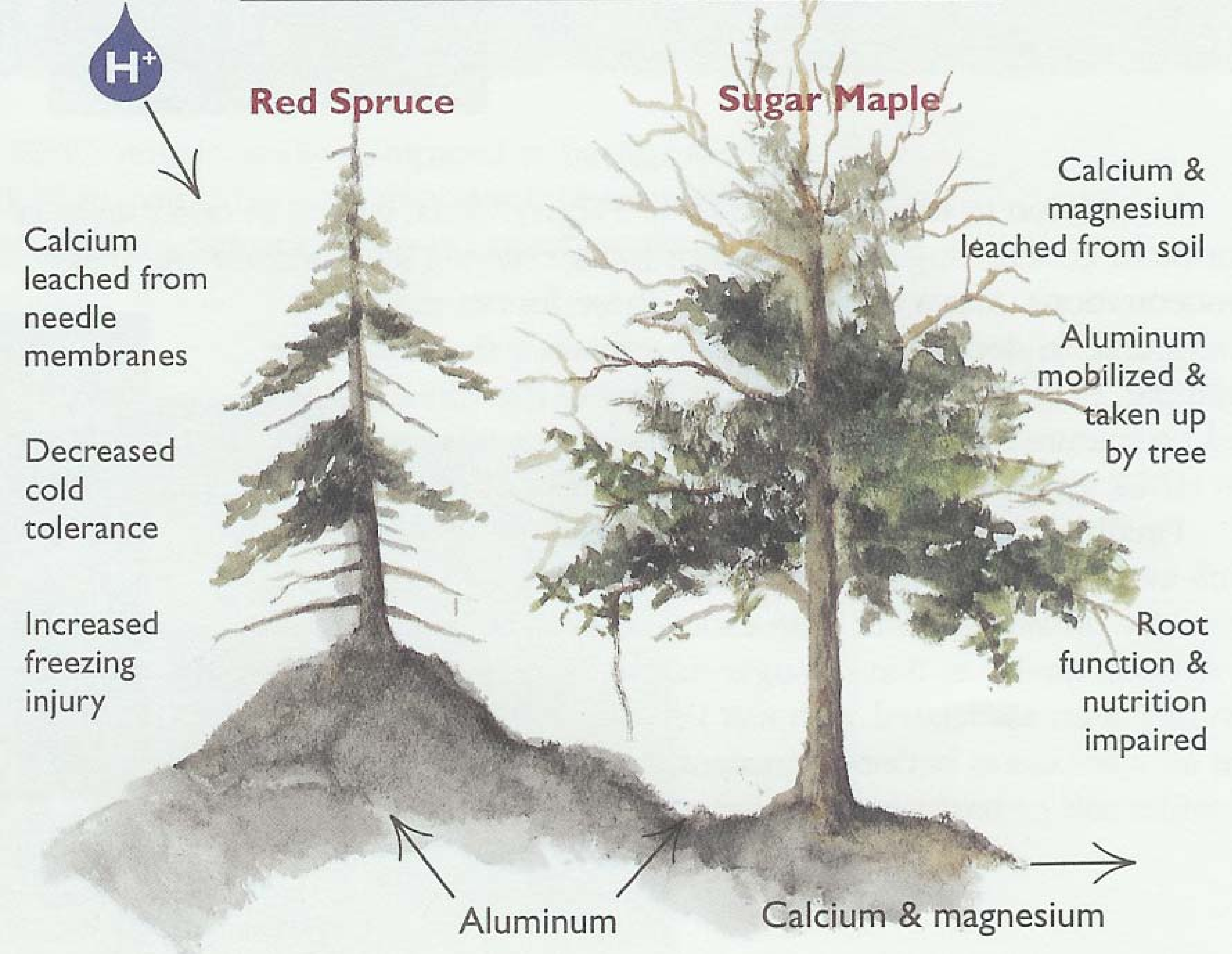


Figure 9. “Acid Rain Revisited.” HBRF

Some processes affecting solute budgets in a catchment

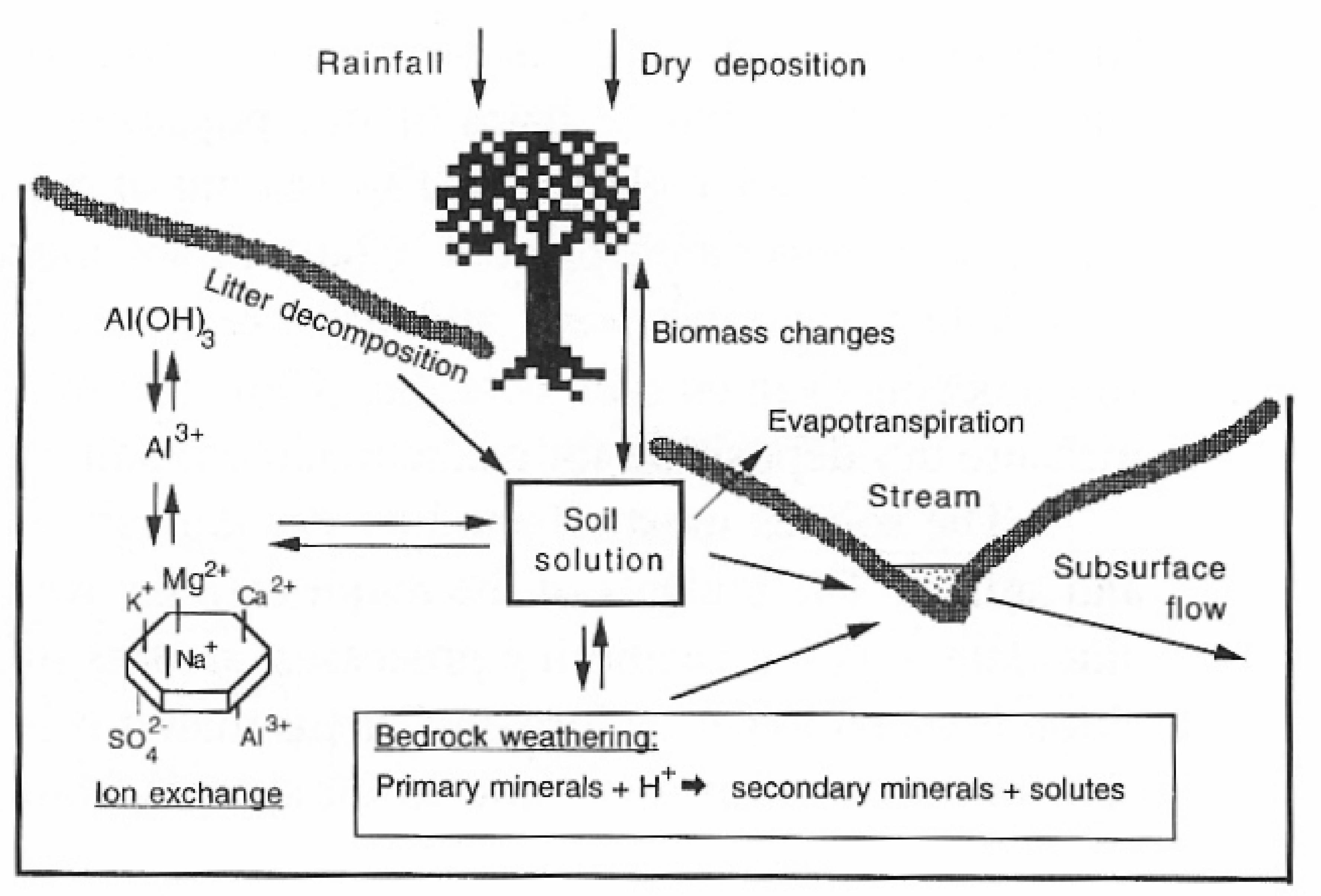


Figure 12-2 Drever, *The Geochemistry of Natural Waters*, 1997

Clay

H+ < --- > Ca^{++} Lose cations

(-) charge of surface attracts cations

Ca is lost to aqueous phase

Clay Mineralogy → Highly charged surface

Cation Exchange Capacity (CEC)

Exchange Sites

Susceptibility of Lakes to Acidification

- Affected areas: * pH<4.5 * relatively small (or zero) fish population.

- It has taken the past 12,000 years to generate soil of the lakes (glaciers scraped it clean to the bedrock).
- High temperature rocks.
  - relatively close to source of SO_2 and NOx (ie. carried to New England, etc. from the Ohio Valley.)

Need to look at:

- Input → Output
- Hydrology → aspect not often understood
- Toxicity → why it affects the fish population
- Geochemical processes → mainly weathering; cation exchange, dissolution, mobilization of Al

Hubbard Brook, New Hampshire

Study from 1963 to present

Driscoll et al. “Changes in the chemistry of surface waters: 25 year results at the Hubbard Brook Experimental Forest, NH.” 1989

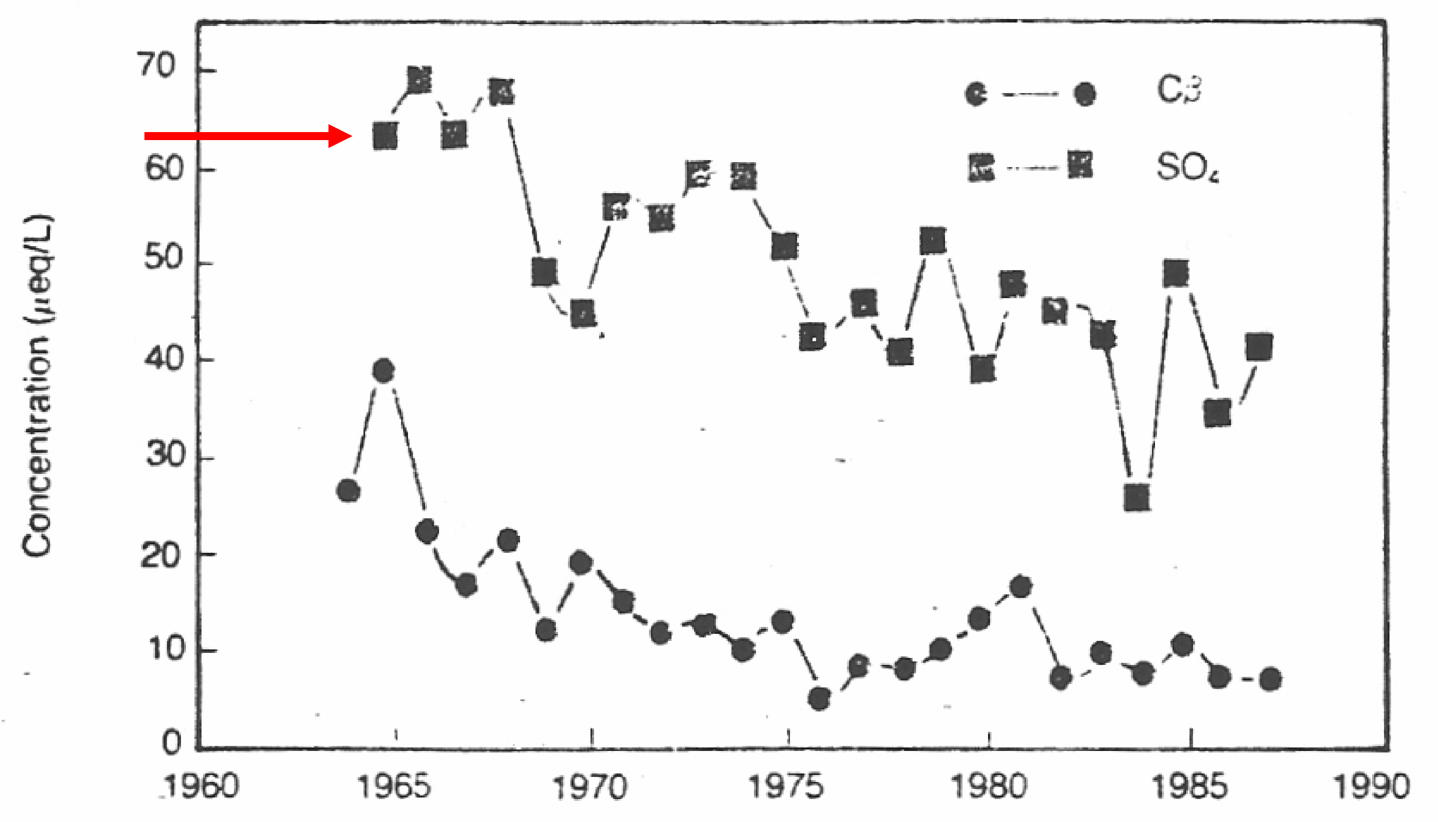
Hubbard Brook, main drainage stream for Hubbard Brook Valley

http://pubs.acs.org/cgi-bin/archive.cgi/esthag/1989/23/i02/pdf/es00179a001.pdf

Upper curve represents the amount of SO_4 (sulfate) present in the rain water in system (SO_4 input dominated by SO_2 input into environment rather than by dust.) H^+ → SO_2.

→ Over time the SO_4 in the rain has dropped from 70 μeq/L (.5 moles of SO_4 ion) over the past 3 years, probably due to the beginning of the Clean Air Act and the beginning of use of low-S coal.

Fig. 1 a) Annual volume weight concentrations of the sum of basic cations (C*β*) and sulfate (SO_4)



Temporal bulk precipitation trends for the reference watershed (number 6) at the Hubbard Brook Experimental

Forest, NH

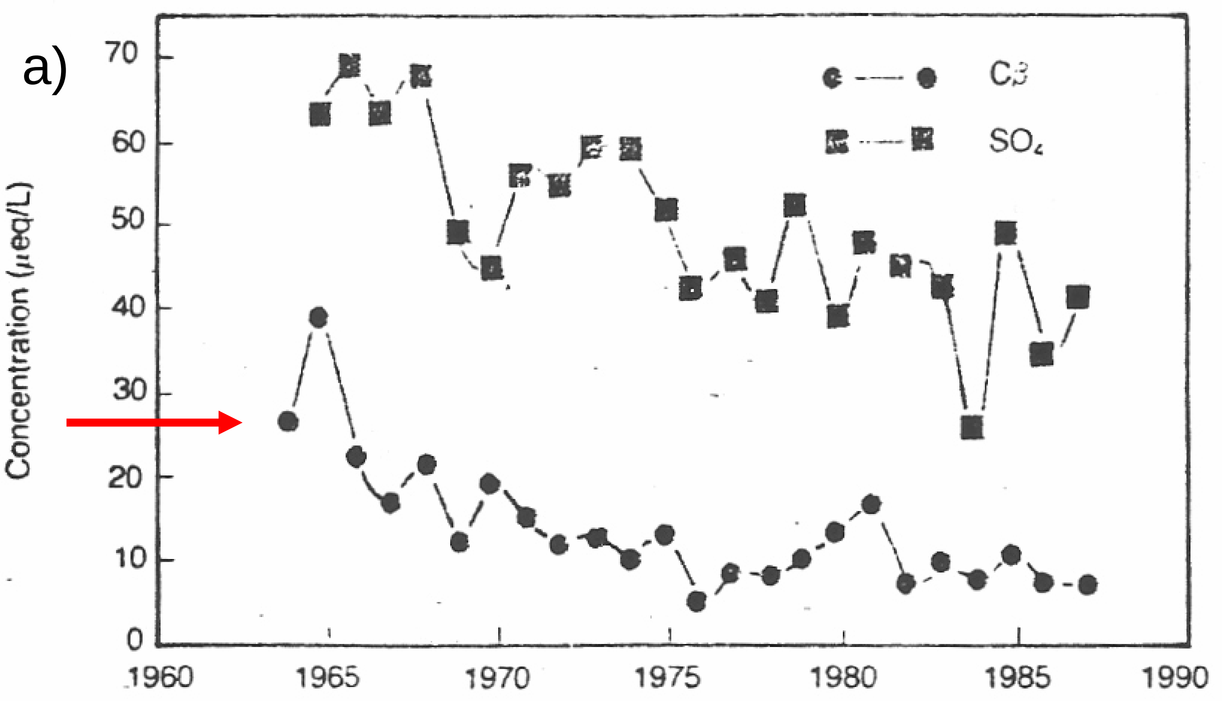
Driscoll, 1989

Lower curve represents the total of base cations (Na, K, Mg, and Ca although we'll focus on Ca). → Moves from 20 to 10µeq/L over the same period of time. The reason for this drop is uncertain; could be a reduction in dust, a change in the amount of rainfall, bad measurements, etc.

* Something has to balance out the difference in SO_4 and cations in charge → H^+

- –[There is about 20µeq/L difference.]
- –H+ 5 x 10-5 moles/L → pH ~4.3.

Driscoll, 1989



Temporal bulk precipitation trends for the reference watershed (number 6) at the Hubbard Brook Experimental Forest, NH. **a) Annual volume weight concentrations of the sum of basic cations (C*β*) and sulfate (SO_4)**

Fig. 1(b) Average precipitation → about a 50% drop in acidity over the years

pH 4.2 → 4.4

→Maybe due to amount of precipitation

→looks as if things are getting better, less acidity that requires neutralization.

Temporal bulk precipitation trends for the reference watershed (number 6) at the Hubbard Brook Experimental

Forest, NH

Driscoll, 1989

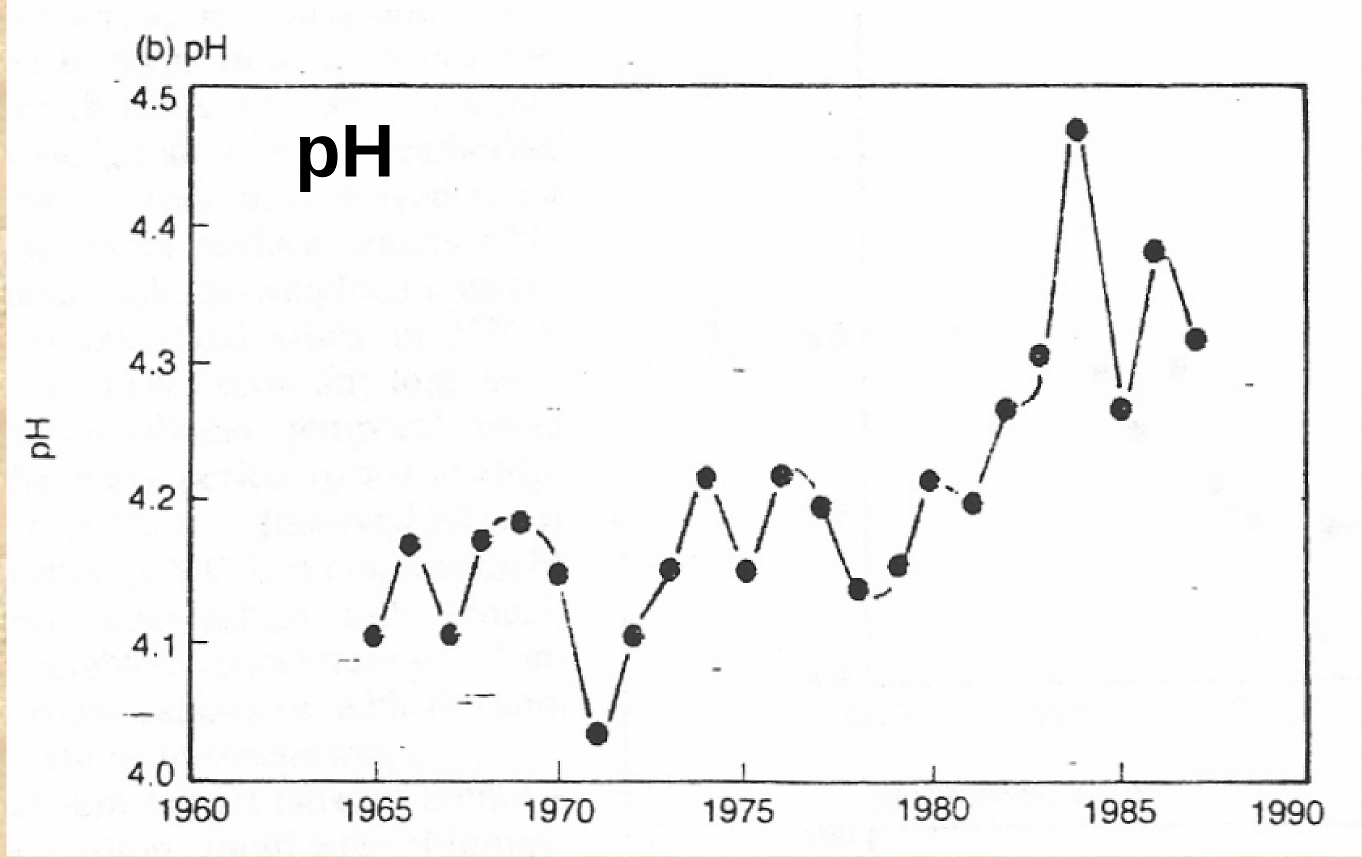
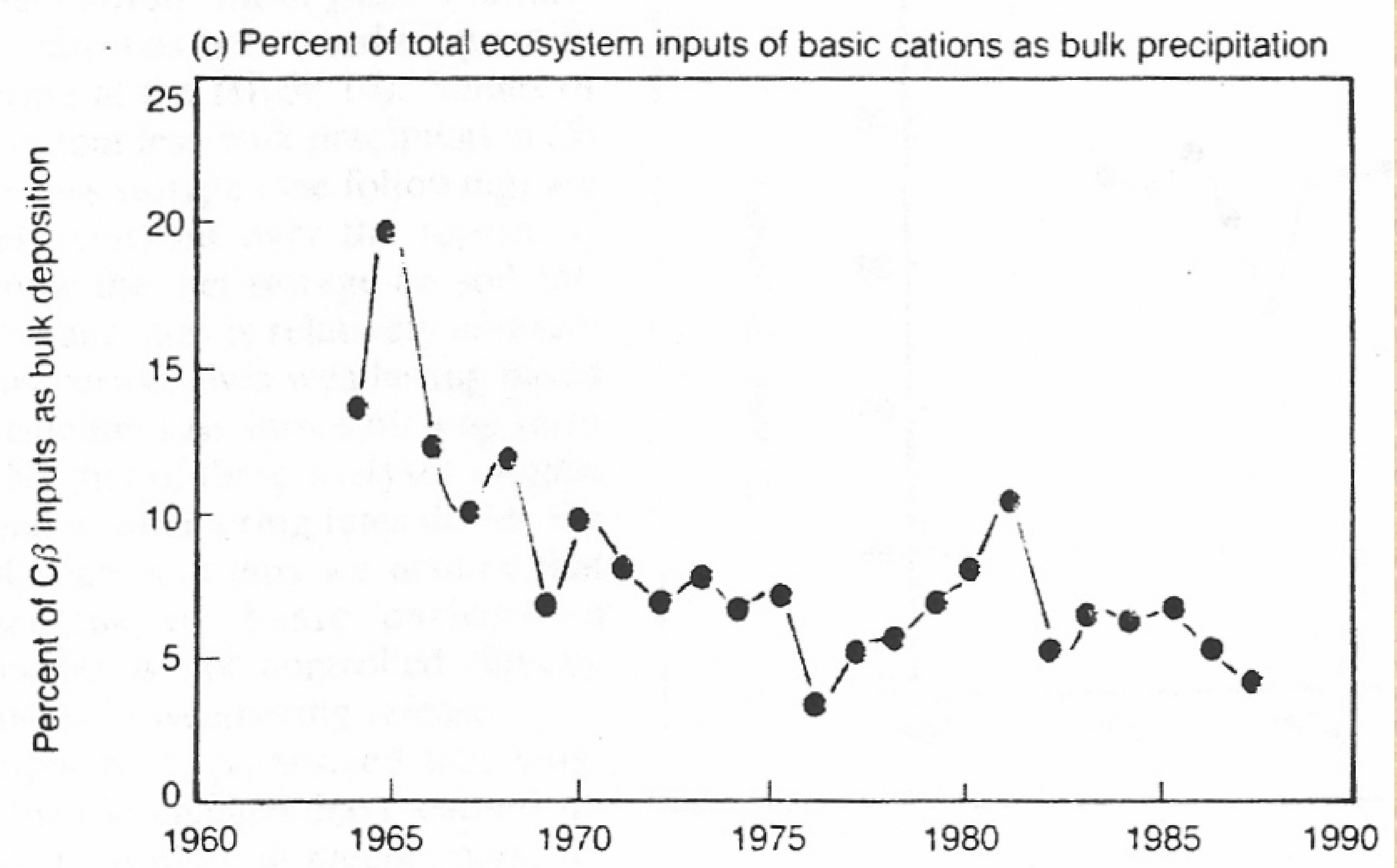


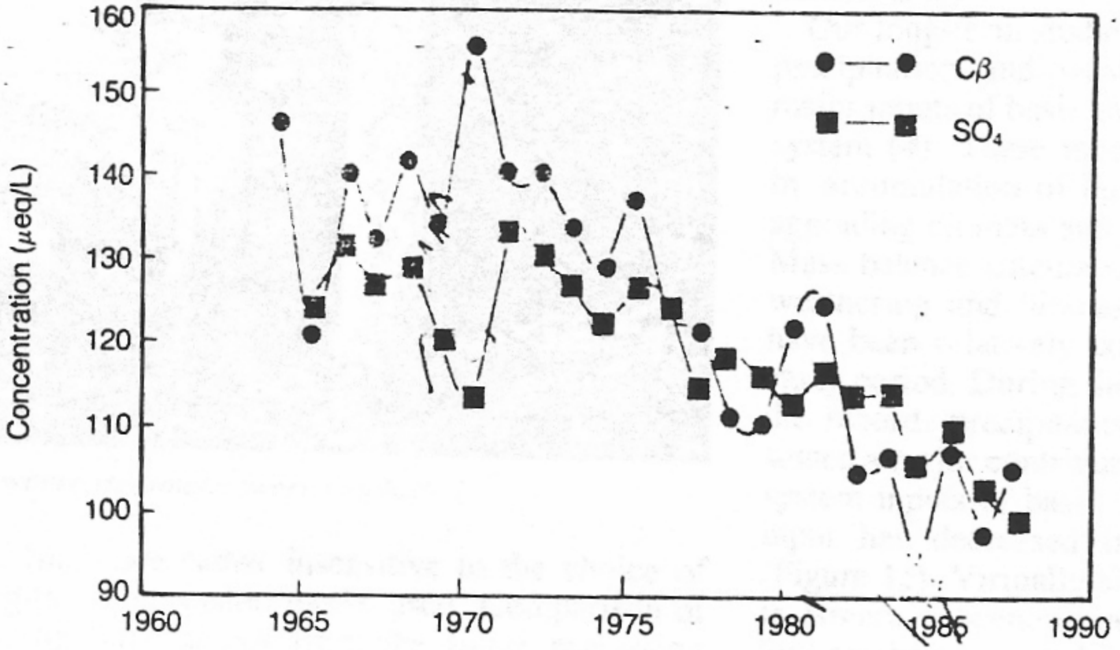
Figure 1(c). Temporal bulk precipitation trends for the reference watershed (number 6) at the Hubbard Brook Experimental Forest, NH



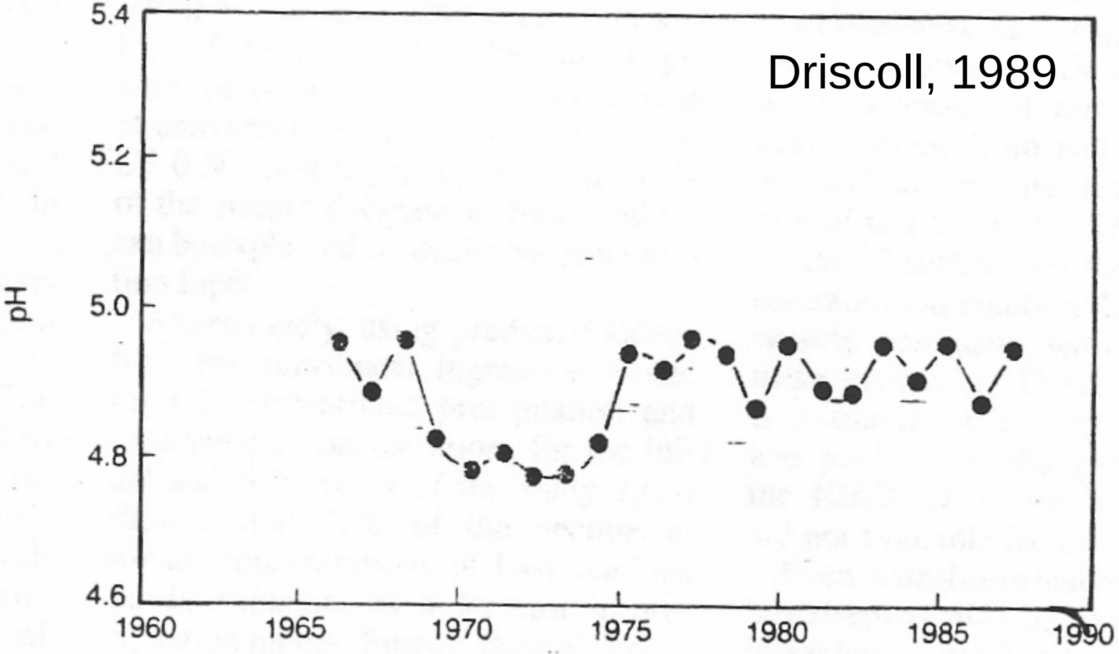
Driscoll, 1989

Figure 2. Temporal streamwater trends for the reference watershed (number 6) at the Hubbard Brook Experimental Forest, NH

(a) Annual, volume-weighted concentrations of the sum of basic cations ($C\beta$) and sulfate (SO_4)



(b) pH



Driscoll, 1989

Fig.2 Output: SO_4 present in stream water→ sum of the base cations are equivalent to the pH→ ~10-5

•factor of 5 lower H^+ acidity than in rainwater.

•→ Therefore, stream water concentrations have been essentially independent of the input**.**

****** something happens between input and output.

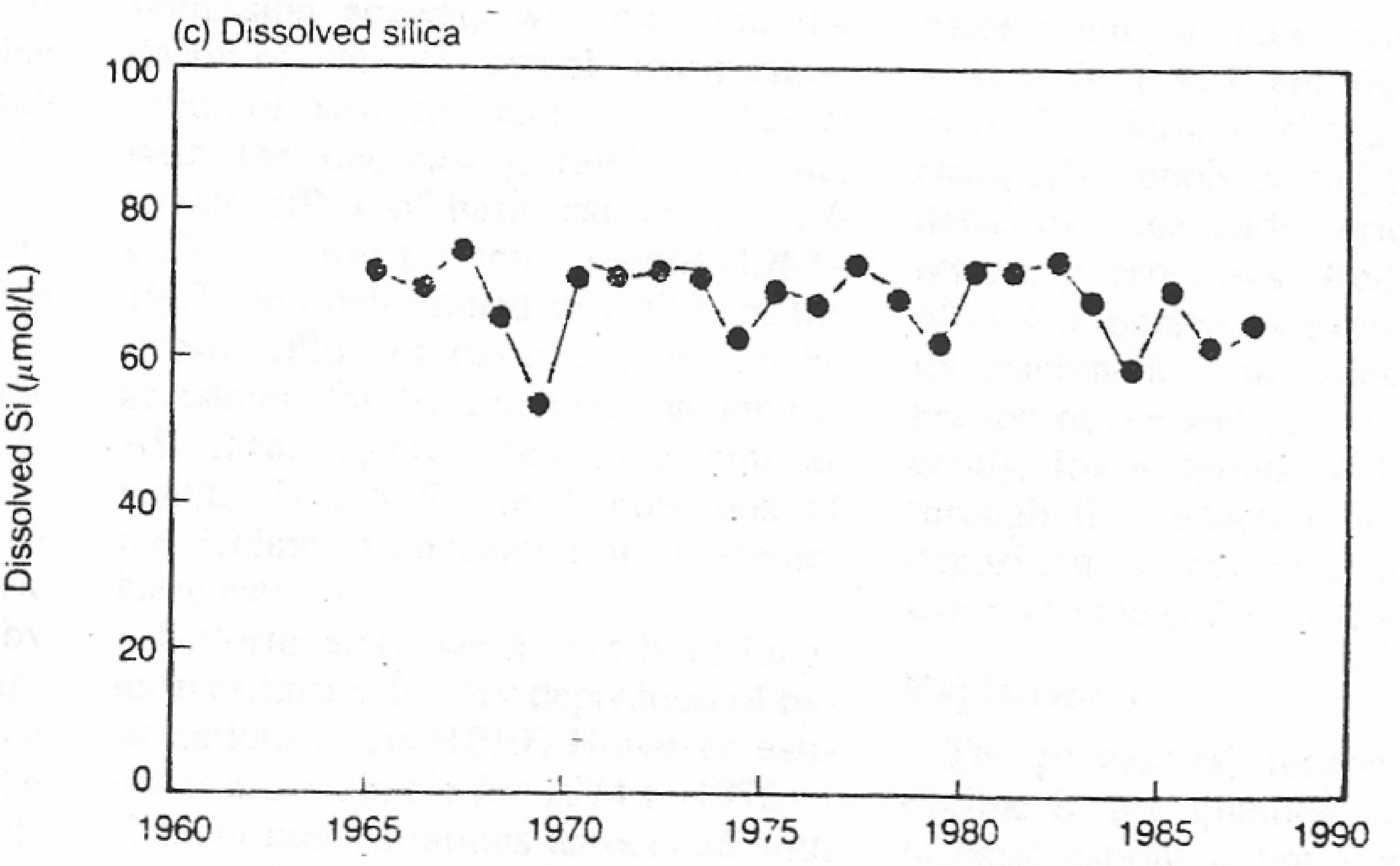
- Overall concentration of SO_4 in rain 70 → 140 in stream
- → this simply reflects that processing has taken place within the watershed.

* Trees exclude SO_4 when taking in water (through evapotranspiration). It can therefore be concentrated in the soil and the remaining water.

→ Only about 50% of the precipitation is discharged into the stream.

* mass balance, 20 - 80% depending on conditions such as temperature, ecosystems, etc.

Figure 2. Temporal streamwater trends for the reference watershed (number 6) at the Hubbard Brook Experimental Forest, NH



Driscoll, 1989

Chemical Response of Lakes in the Adirondack Region of New York to Declines in Acidic Deposition

CHARLES T. DRISCOLL, KIMBERLEY M. DRISCOLL, KAREN M. ROY, AND MYRON J. MITCHELL§

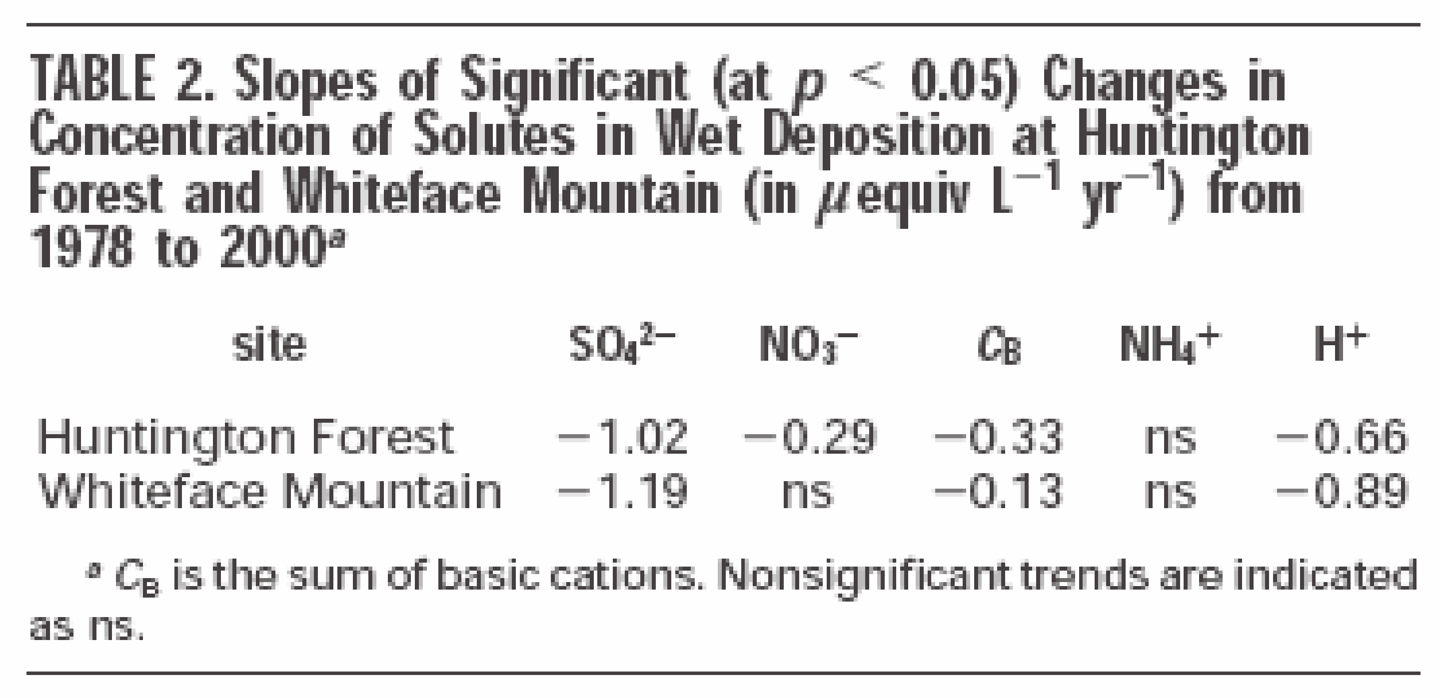


TABLE 2. Slopes of Significant (at $p < 0.05$) Changes in Concentration of Solutes in Wet Deposition at Huntington Forest and Whiteface Mountain (in μequiv L^{-1} yr^{-1}) from 1978 to 2000[a]

site	SO_4^{2-}	NO_3^-	C_B	NH_4^+	H^+
Huntington Forest	−1.02	−0.29	−0.33	ns	−0.66
Whiteface Mountain	−1.19	ns	−0.13	ns	−0.89

[a] C_B is the sum of basic cations. Nonsignificant trends are indicated as ns.

http://pubs.acs.org/cgi-bin/article.cgi/esthag/2003/37/i10/pdf/es020924h.pdf

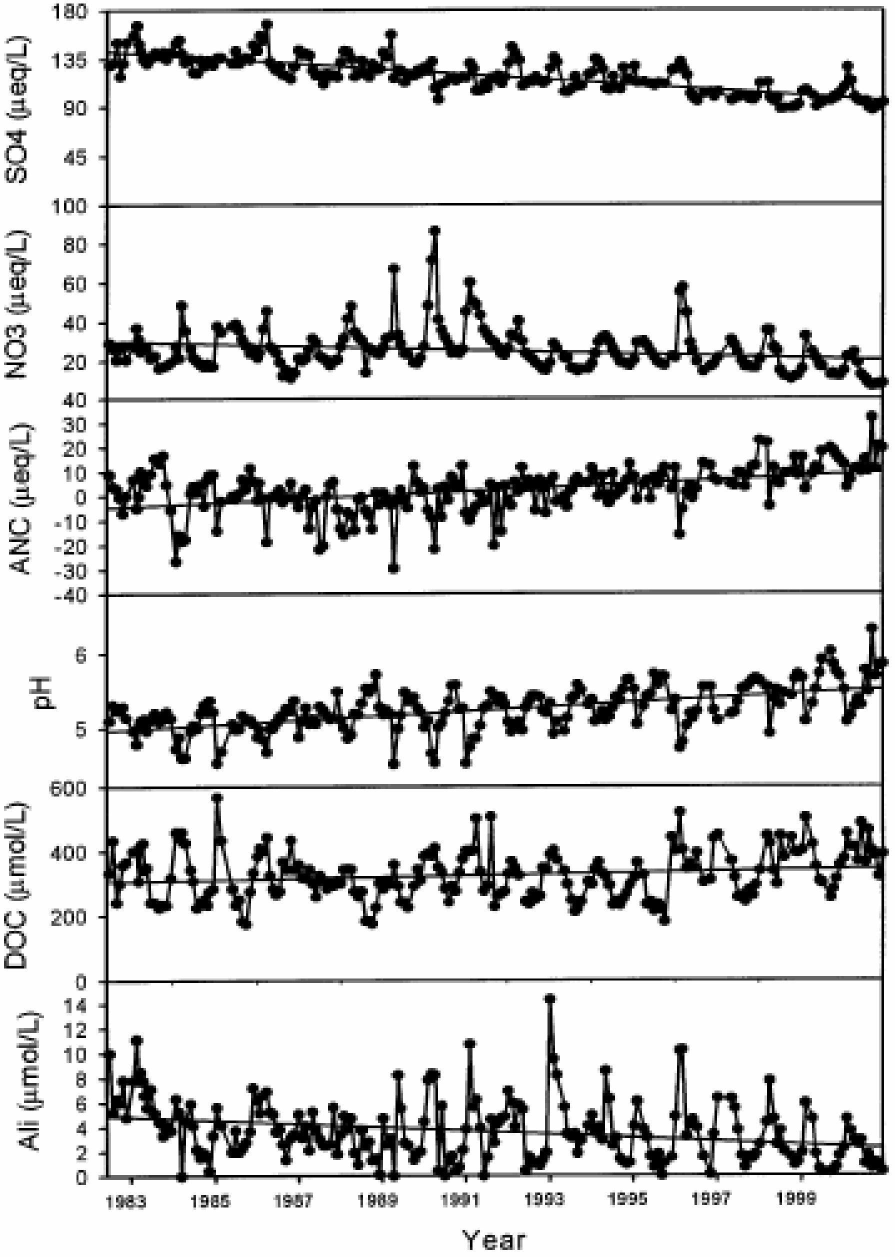


FIGURE 1. Concentrations of SO_4^{2-} (a), NO_3^- (b), acid-neutralizing capacity (ANC; c), pH (d), dissolved organic carbon (DOC; e), and monomeric Al (f) in Big Moose Lake. A significant trend is indicated by a line.

http://pubs.acs.org/cgi-bin/article.cgi/esthag/2003/37/i10/pdf/es020924h.pdf

Calcium and potassium fluxes at the Hubbard Brook Experimental Watershed

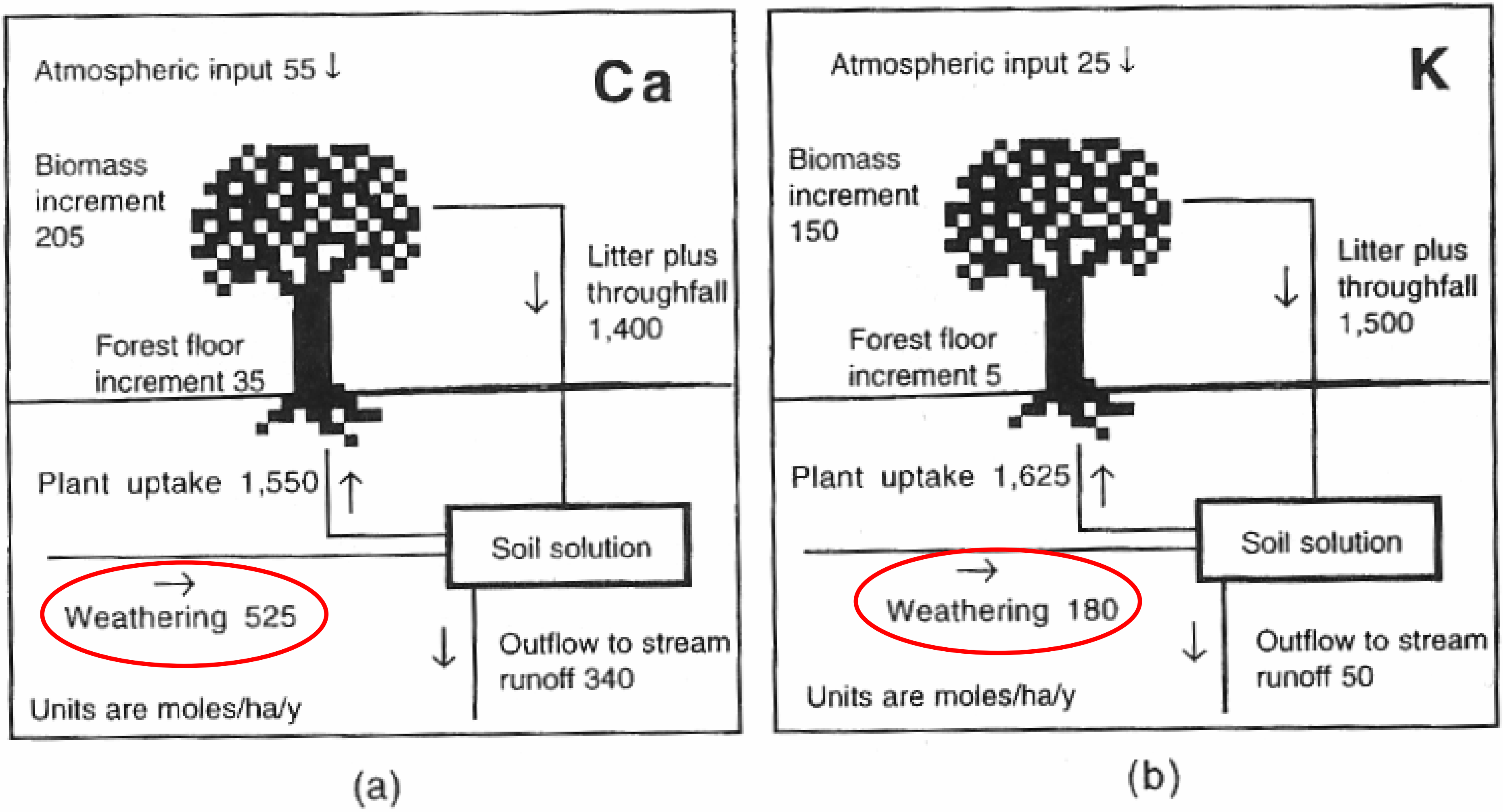


Figure 12-3 Drever, *The Geochemistry of Natural Waters*, 1997

Clay

H+ < --- > Ca^{++} Lose cations

(-) charge of surface attracts cations

Ca is lost to aqueous phase

Clay Mineralogy → Highly charged surface

Cation Exchange Capacity (CEC)

Exchange Sites

[10-3 moles of charge] meq = milliequivalents

Smectites ---> 1 meq/g

Don't see much around here--> result of the weathering of volcanics

[volcanic glass]

Illites ---> 50 - 500µeq/g

~ 80% muscovite; 20% smectite → varied, non-unique mixed structures

Kaolinite ---> 10 µeq/g

$Al_2Si_2O_5(OH)_4$ - low exchange capacity because no cations in its structure. Small surface charge.

Clays: lose cations.   *** Surface phenomena

→ In smectites and illites, with high exchange capacity, attracts a cation to the surface which is bound only by an *electrostatic charge*.

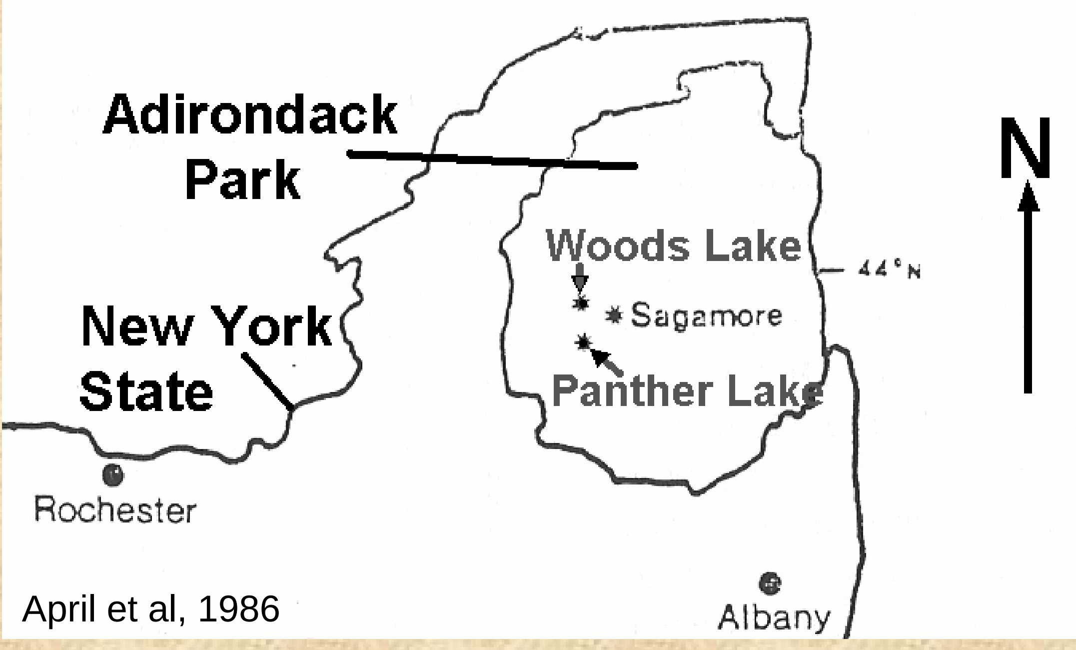
** Surfaces of clays can be highly charged, and different clays have different abilities to exchange.

Look at 2 systems:

- Woods Lake pH~ 4.3
- Panther Lake pH ~ 6

Both of these lakes have the *same input*, therefore the difference in pH is mostly due to hydrology and the capacity of the systems.

http://www.adirondacklakessurvey.org/pics/woods1.html



April et al, 1986

Panther Lake:

- Glacial till (Glaciers scraped crystalline rocks clean)
- Much of water doesn't flow directly into the lake but goes into watershed.
- Thick core about 10 meters of soil which overlies bedrock.
- Water will flow to lake due to hydraulic head(flows from higher pressure to lower pressure; difference in pressures due to the differences in the elevation of the water.)

Panther Lake:

***** Only a certain percentage will be as a base flow (along flow lines)

* Some percentage will be overland flow, surface runoff.

→ This dominantly happens in the spring where the snow is melting but the ground is still frozen. More water will go overland to the lake. In the spring, the pH will even drop from 6 to 5 because the pH of snow is about 4 and a higher percentage goes directly there rather than being processed in the watershed first.

Woods Lake:

- right on crystalline rocks with a thin soil cover of only about 1 meter; pH about 4.3
- Much of the flow is overland or through the O-horizon (surface layers)

Interflow → just below the surface, fairly permeable O-horizon.

http://www.adirondacklakessurvey.org/pics/woods1.html

http://www.oldforgecruises.com/lollie/scenic.htm

- Lakes formed 12,000 years ago with retreat of glaciers therefore know time that the lakes started.
- Assume that the composition of till is about constant.

How much Ca is present as a function of depth? (See Figure 2).

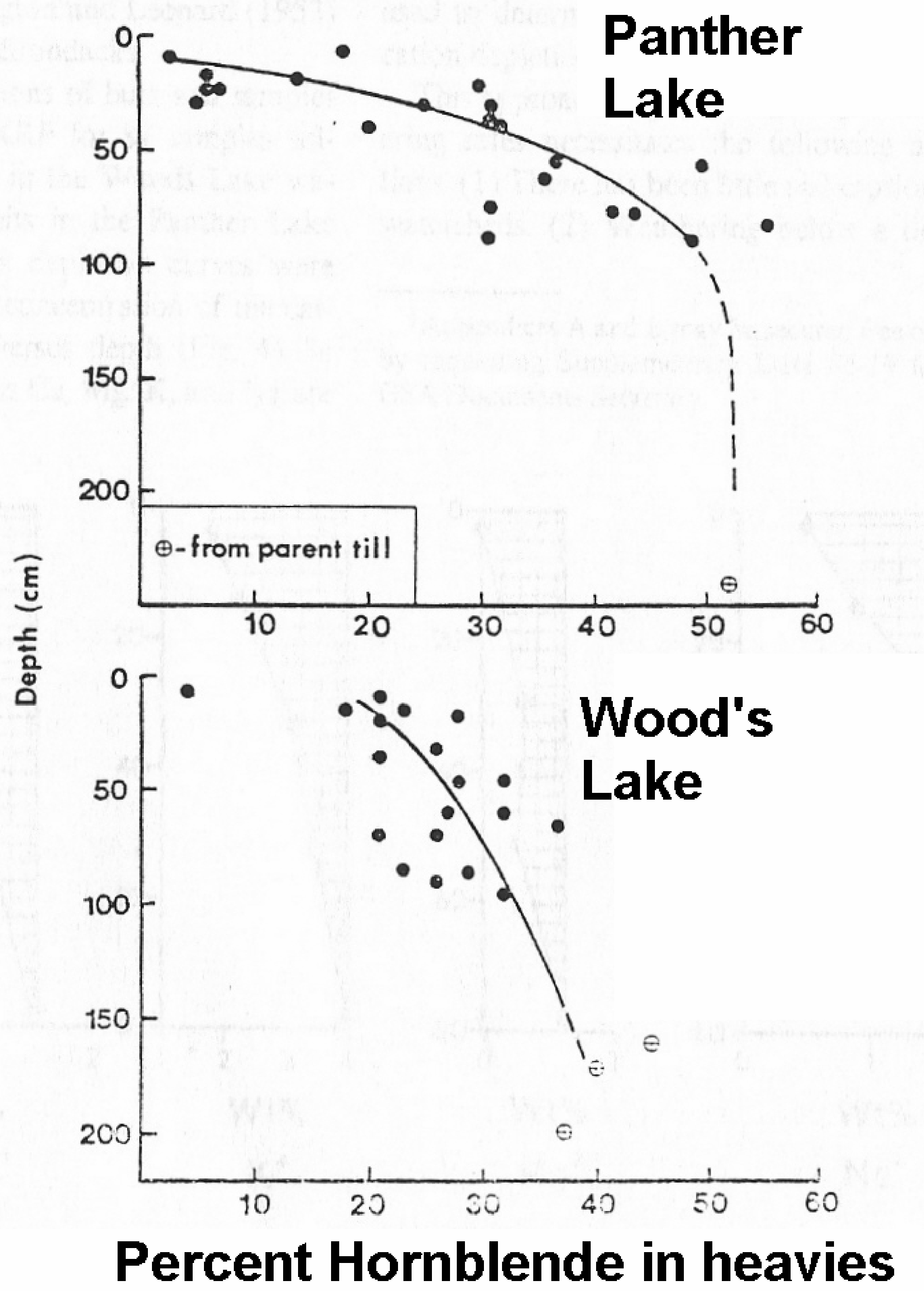


Figure 2. Trends in hornblende abundance with depth in Panther Lake and Woods Lake watershed soil profiles

After 10 meters, it is about constant -- hitting bedrock which is probably granite or granite gneiss.

- Weathering in the upper zone has removed cations. The weathering does slowly break down the bedrock to release cations available for exchange.

April et al, 1986

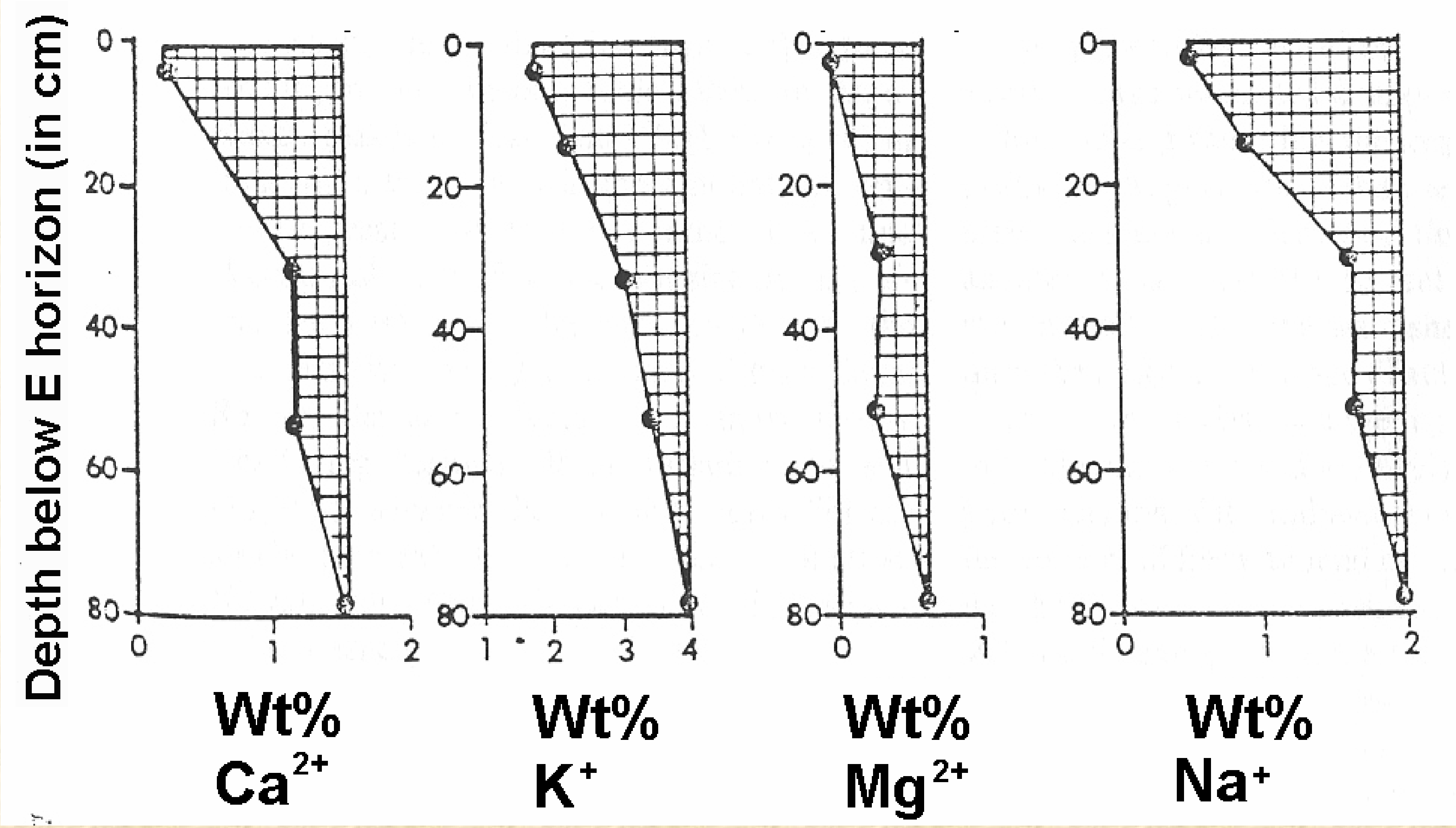


Figure 4. Example of cation-depletion curves constructed for soils in Panther Lake watershed.

April et al, 1986

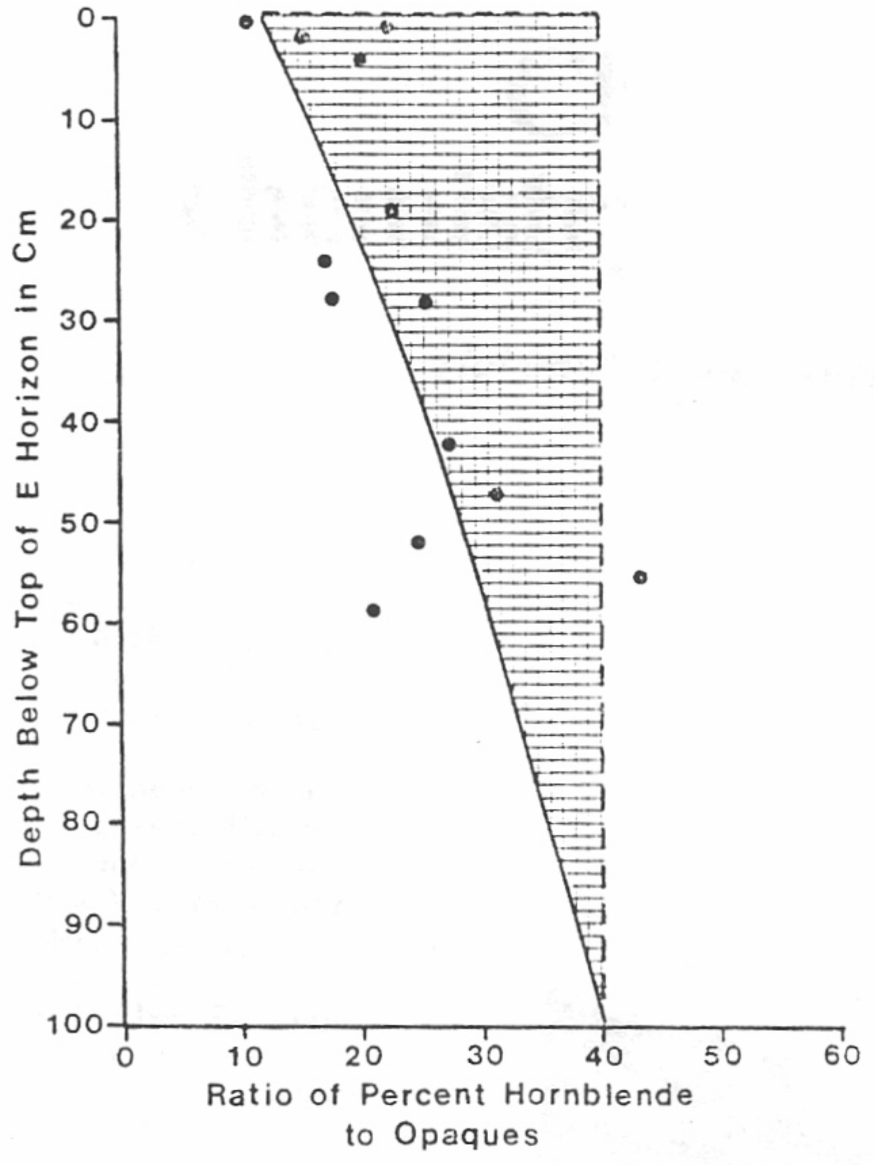


Figure 5. Hornblende depletion curve constructed for Woods Lake watershed, showing the integrated area used to calculate a weathering rate in grams of hornblende/ha·yr

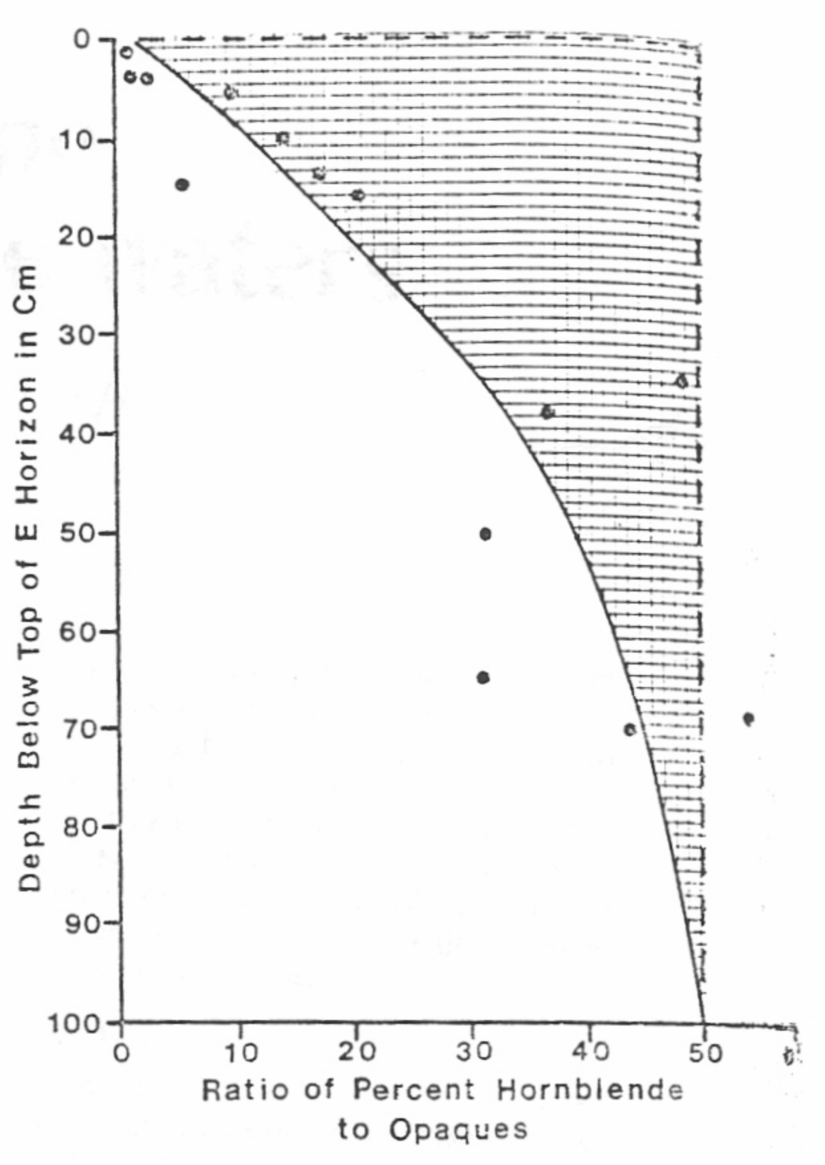


Figure 6. Hornblende depletion curve constructed for Panther Lake watershed, showing the integrated area used to calculate a weathering rate in grams of hornblende/ha·yr

April et al, 1986

	Panther Lake	**Woods Lake**
Till thickness	8 m	1 m
Net output of Ca2+	1200 eq/ha/yr	150 eq/ha/yr
Long term weathering	500 eq/ha/yr	600 eq/ha/yr
Acid input	~1200 eq/ha/yr	~ 1200 eq/ha/yr

- Long term weathering rate → close in both lakes, about 600eq/ha/year.
- But Panther has much less acid. Why?
- Wood's Lake → **comparable weathering rate but the residence time is not sufficient for the exchange reactions to occur**.

Look at relative rates, mass balance.

Therefore, we need to examine the effect of soil-

- Amount of acidity input is the same ~1200eq/hectare (= 100 x 100 meters)/year
- There is a large clay component in soils

  →these clays have lost a cation (to water) and therefore have a net negative charge.

They will then attract cations.

- Illites -Upstate New York -- temperate latitudes
  - composed of about 80% muscovite (with a low cation exchange capacity) and about 20% smectite (with a high cation exchange capacity). These percentages are highly variable and illites are relatively ill-defined.

Clay

H+ < ---Al^{3+} ---> Ca^{++} Lose base cations

(-) charge of surface attracts cations

Ca is lost to aqueous phase

Clay Mineralogy → Highly charged surface

Cation Exchange Capacity (CEC)

Exchange Sites

[10-3 moles of charge] meq = milliequivalents

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Don't see much around here--> result of the weathering of volcanics

[volcanic glass]

Illites ---> 50 - 500μeq/g

~ 80% muscovite; 20% smectite → varied, non-unique mixed structures

Kaolinite ---> 10 μeq/g

$Al_2Si_2O_5(OH)_4$ - low exchange capacity because no cations in its structure. Small surface charge.

Clays: lose cations.   *** Surface phenomena

→ In smectites and illites, with high exchange capacity, attracts a cation to the surface which is bound only by an *electrostatic charge*.

** Surfaces of clays can be highly charged, and different clays have different abilities to exchange.

- 1. Lack of $CaCO_3$
- 2. Thin or no soil = high surface flow into lakes

3. Thick soil: large exchangeable pool of Ca^{2+}

Review of Equilibrium:

$xA + yB \rightarrow zC + wD$ $\quad K_{eq} = \frac{[C]^z[D]^w}{[A]^x[B]^y} \quad = 10^{-5.6} \rightarrow pK = 5.6$

Acid : $\quad HaC \leftrightarrow H^+ + Ac^-$ $\quad K_{eq} = \frac{[H^+][Ac^-]}{[Hac]} \quad [Ac^-] = 10^{-7.3}$

$[H_2CO_3] = k_T \, P_{CO2}$ $\quad$ at $P_{CO2} = 10^{-3.45}$ $\quad [H_2CO_3] = 10^{-5}$ M

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ $\quad k = 10^{-1.55}$

$pk_1 = +5.7$ $\quad H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ $\quad k_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$

$10^{-9.2} = 10^{-10.7} = [H^+][HCO_3^-]$

$[HCO_3^-] = [H^+] = 10^{-5.4} \rightarrow pH = 5.4$ $\quad k_1 = 10^{-5.7}$

Soil P_{CO2} ~ 10,000 ppm $\rightarrow 10^{-2} \rightarrow$ pH~4.6

$$K_{Gibbsite} \text{ (equilibrium constant)} = 10^{8.1} \text{ ---> } \frac{a \text{ (activity)}Al^{3+}}{a \text{ (activity)}H^{+}} = \frac{10^{-7} \text{ moles/L}}{10^{-5} \text{ moles/L}}$$

$\underline{10^{-4} \text{ moles/L}}$ quite high

10^{-4} moles/L (pH=4)

→ amount of Al present in solution is a very strong function of pH.

* Change of pH of 1 unit will produce a change of 10^3 change in Al, 3:1 ratio

- **pH<6, dominant species of Al is Al^{3+}**
- In basic solutions, others are dominant ($Al(OH)_4$ - Aluminum hydroxide)
  - whole series of hydroxide complexes of Al (Al- complexes)

Al Complexes:

$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$

$Al^{3+} + 2H_2O \rightarrow Al(OH)_2^{+} + 2H^+$

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

$Al^{3+} + 4H_2O \rightarrow Al(OH)_4^{-} + 4H^+$

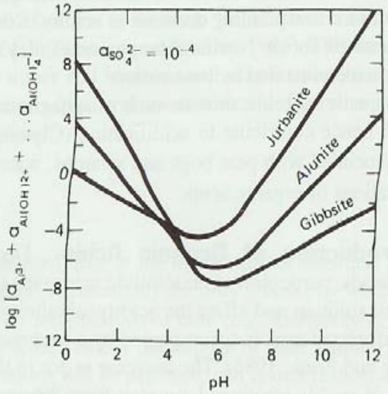
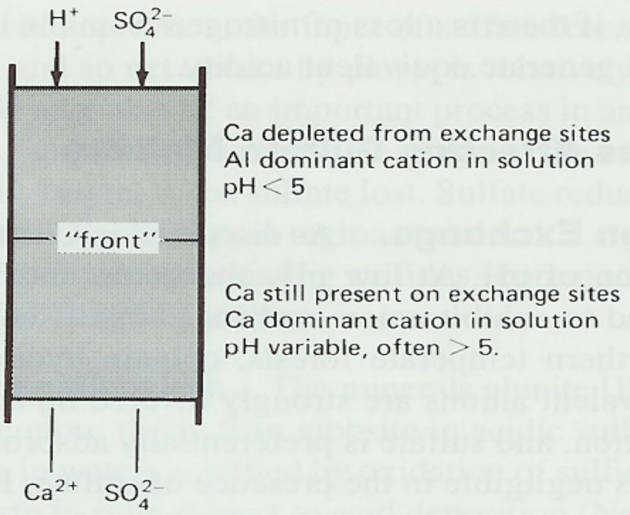


FIGURE 13-7 Solubility curves for gibbsite, alunite, and jurbanite at sulfate and potassium activities of 10^{-4} (solubility of alunite is relatively insensitive to K^+ activity, even though it contains K) (after Nordstrom, 1982).

- As the water moves down, H^+ exchanges with Ca^{++}
- When the calcium is depleted, then the H+ begins to dissolve Al^{3+} (which is normally very stable in soil (as $Al(OH)_3$ Gibbsite) but is soluble under acid conditions). $3H^+ + Al(OH)_3 = Al^{3+} + 3H_2O$
- As the water continues down the column and reaches an area where the Ca^{2+} has not been depleted (at the front) then the Ca and Al^{3+} exchange the water becomes calcium sulfate.
- $3Ca(adsorbed) + 2Al^{3+} (aq) = 3Ca^{++} (aq) + 2\ Al(adsorbed)$

$H_2SO_4 \rightarrow Ca^{++} + SO_4^{--}$ pH>5 (near neutral)

FIGURE 13-6 Soil column affected by simulated acid deposition.



Hydrology

How could it play a role? → surface runoff, base flow

Base Cations in Exchangeable Sites

→ Thickness of soil layer

- Dissolution of Gibbsite , Kaolinite
- \- Ion Exchange

Model: $\frac{E_{Al}^2}{E_{Ca}^3} = K_{ex} \frac{a^2_{Al3+}}{a^3_{Ca2+}}$

$\%Al\ (eq) = \frac{3m_{Al3+}}{2m_{Ca2+} + 3m_{Al3+}}$

Acid Input (H_2SO_4, HNO_3)

- Thick soil → H^+ exchanges w/ Ca^{2+} ; H^+ dissolves $Al(OH)_3^-$
  - $CaCO_3$ causes neutralization

- Thin or no soil (size of watershed) ~ soil buffer?
- Acid Lake Condition (bathtub) -- directly on lake

Hydrology

How could it play a role? → surface runoff, base flow

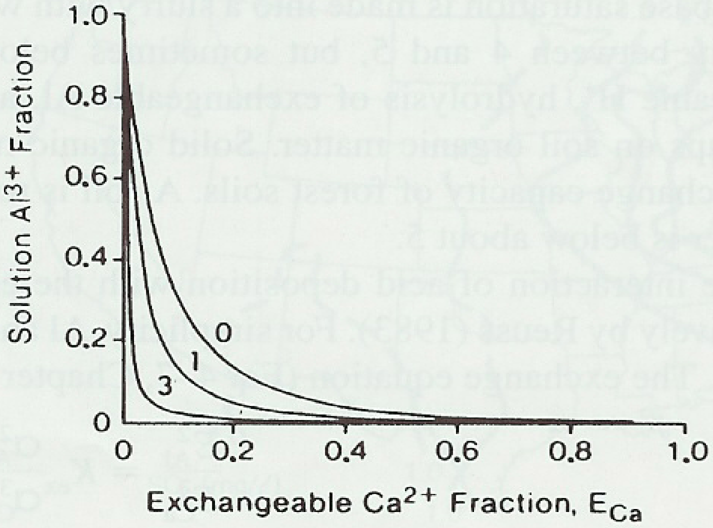
- Base Cations in Exchangeable Sites→ Thickness of soil layer

Dissolution of Gibbsite

- - Ion Exchange

Model: $\frac{E_{Al}^{2}}{E_{Ca}^{3}} = K_{ex} \frac{a^{2}_{Al3+}}{a^{3}_{Ca2+}}$ $\%Al\ (eq) = \frac{3m_{Al3+}}{2m_{Ca2+} + 3m_{Al3+}}$

FIGURE 13-5 Relationship between ratio of Al to Al + Ca in solution and ratio of Ca to Al + Ca on exchange sites (both in units of equivalents of charge) for different values of the exchange constant, log K_{ex} (after Reuss, 1983).



→ As the system receives more and more acid, the front will move further down until all the Ca is depleted from the system -- will have used up all the Ca ions.

(front = boundary between no available and available Ca)

*charge neutrality must be maintained.

- Front will continue to drop
- At some point the Al^{3+} will be present in solution to the lake

$Al(OH)_3 + 3H^+ \text{ ---> } Al^{3+} + 3H_2O$

* Generally, solutions in soils are in equilibrium will gibbsite, although it can't be found directly in the soil. But reasonable assumption is that generally, reactions are controlled by gibbsite.

$K_{Gibbsite}$ (equilibrium constant) = $10^{8.1}$ ---> $\dfrac{\text{a (activity)}Al^{3+}}{a^{3}\text{(activity)}(H^{+})}$ = $\dfrac{10^{-7}\text{ moles/L}}{10^{-5}\text{ moles/L}}$

$\dfrac{10^{-4}\text{ moles/L}}{10^{-4}\text{moles/L}}$ quite high

→ amount of Al present in solution is a very strong function of pH.

* Change of pH of 1 will produce a change of 1 x 10^3 change in Al, 3:1 ratio

- **pH<6, dominant species of Al is Al^{3+}**
- In basic solutions, others are dominant ($Al(OH)_4$ - Aluminum hydroxide)
  - whole series of hydroxide complexes of Al (Al- complexes)

Al Complexes:

$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$

$Al^{3+} + 2H_2O \rightarrow Al(OH)_2^{+} + 2H^+$

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

$Al^{3+} + aH_2O \rightarrow Al(OH)_2^{-} + aH^+$

So what happens to the fish?

Al is stable in acid water.

→But the way fish get oxygen is by passing water over their gills, which are essentially neutral. **When the Al gets there the Al^{3+} is oxidized to Al hydroxide and coats the gills, which suffocates the fish.** Therefore you get acid lakes without fish.

	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	🟥	🟥	🟥			

http://www.epa.gov/airmarkets/acidrain/effects/surfacewater.html

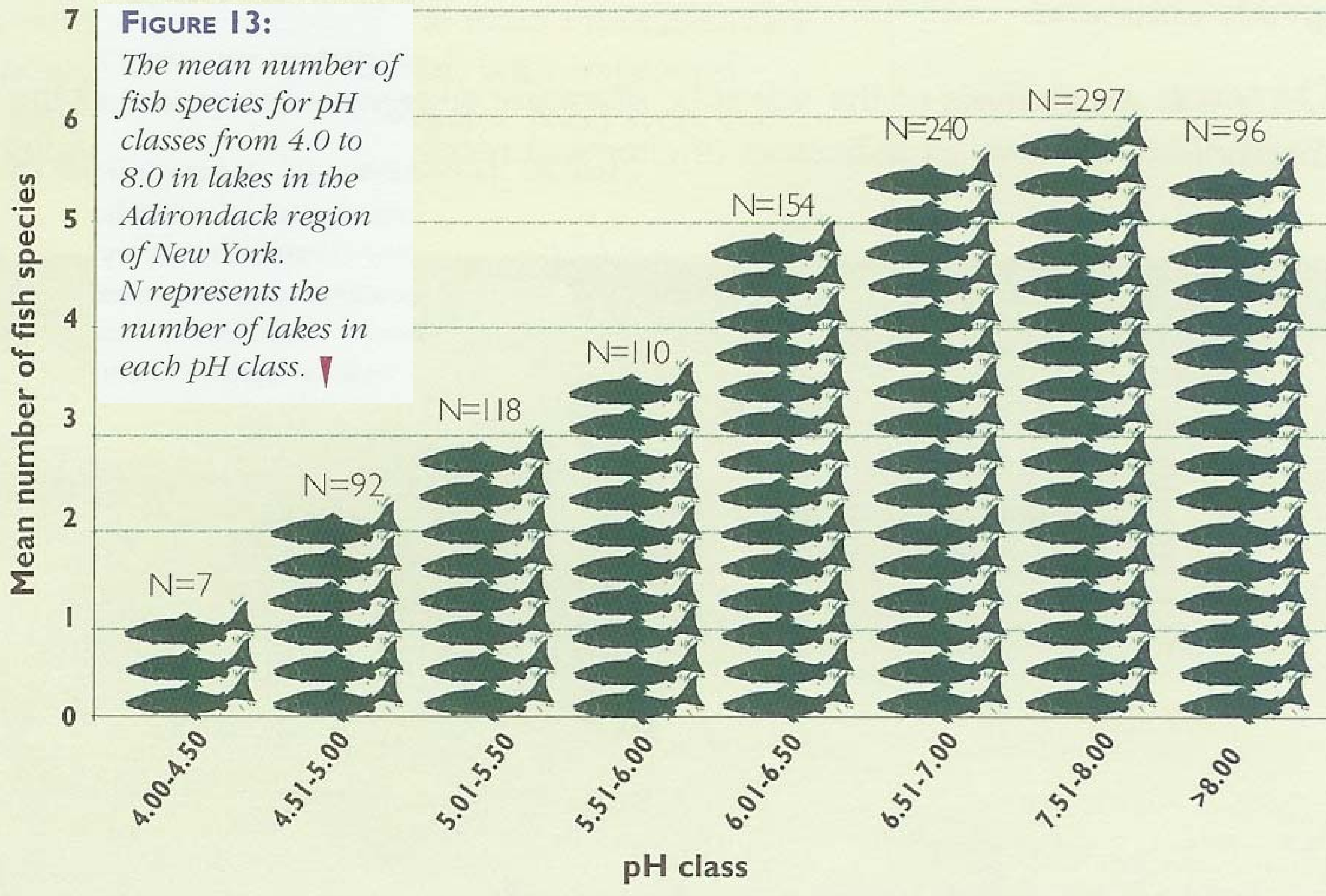
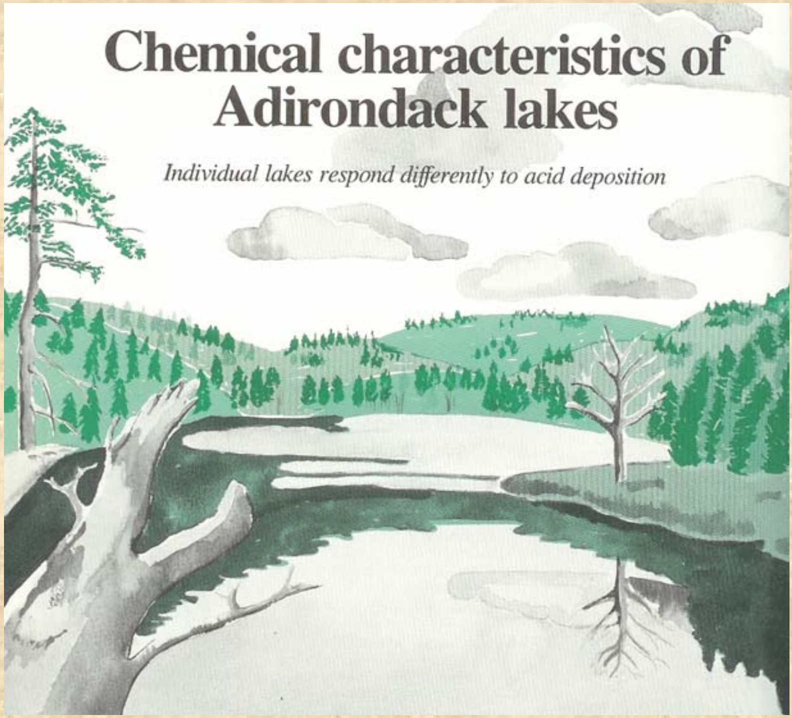


FIGURE 13:
The mean number of fish species for pH classes from 4.0 to 8.0 in lakes in the Adirondack region of New York. N represents the number of lakes in each pH class.

Figure 13. “Acid Rain Revisited.” HBRF



Chemical characteristics of Adirondack lakes

Individual lakes respond differently to acid deposition

Driscoll and Newton, 1985

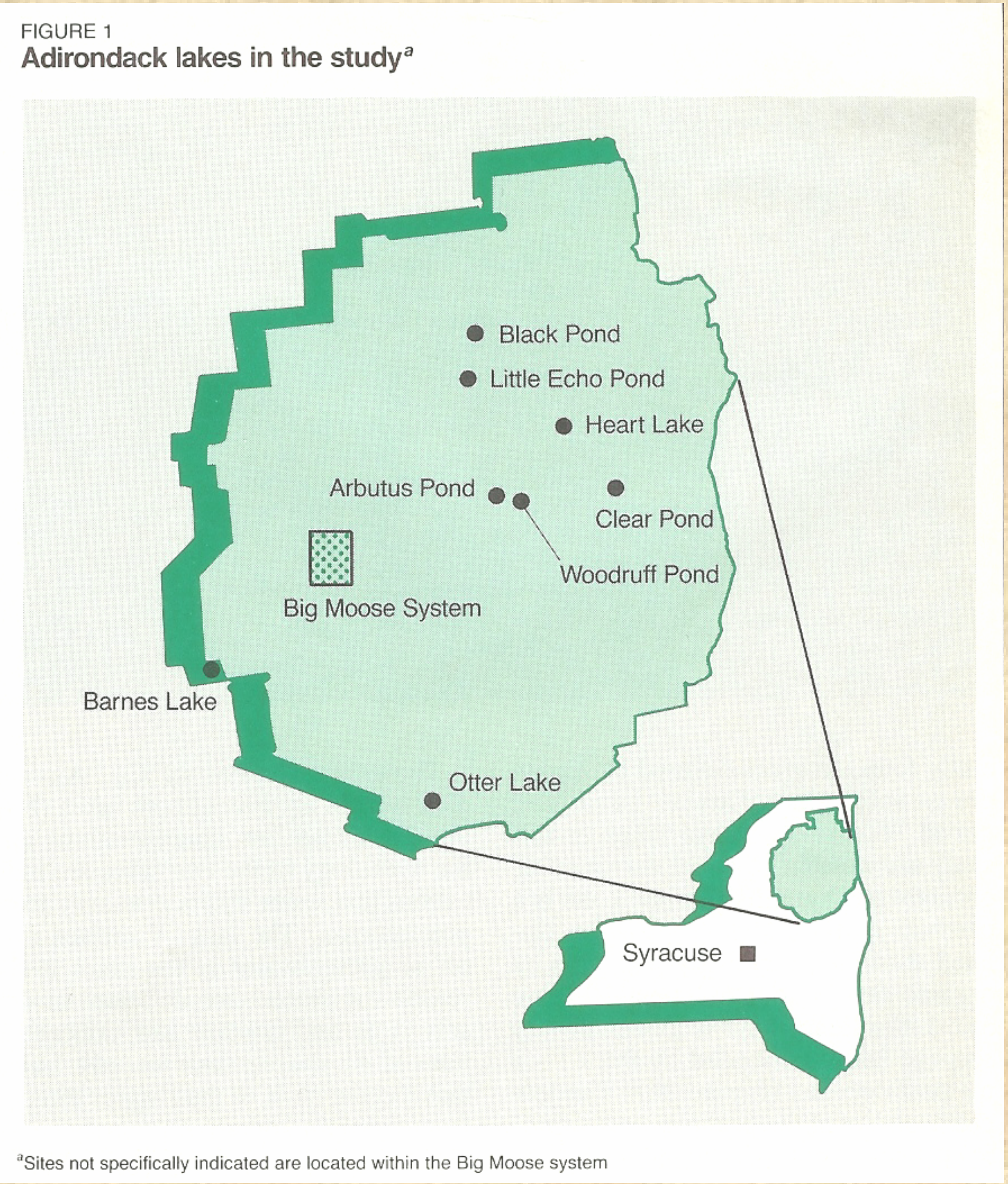
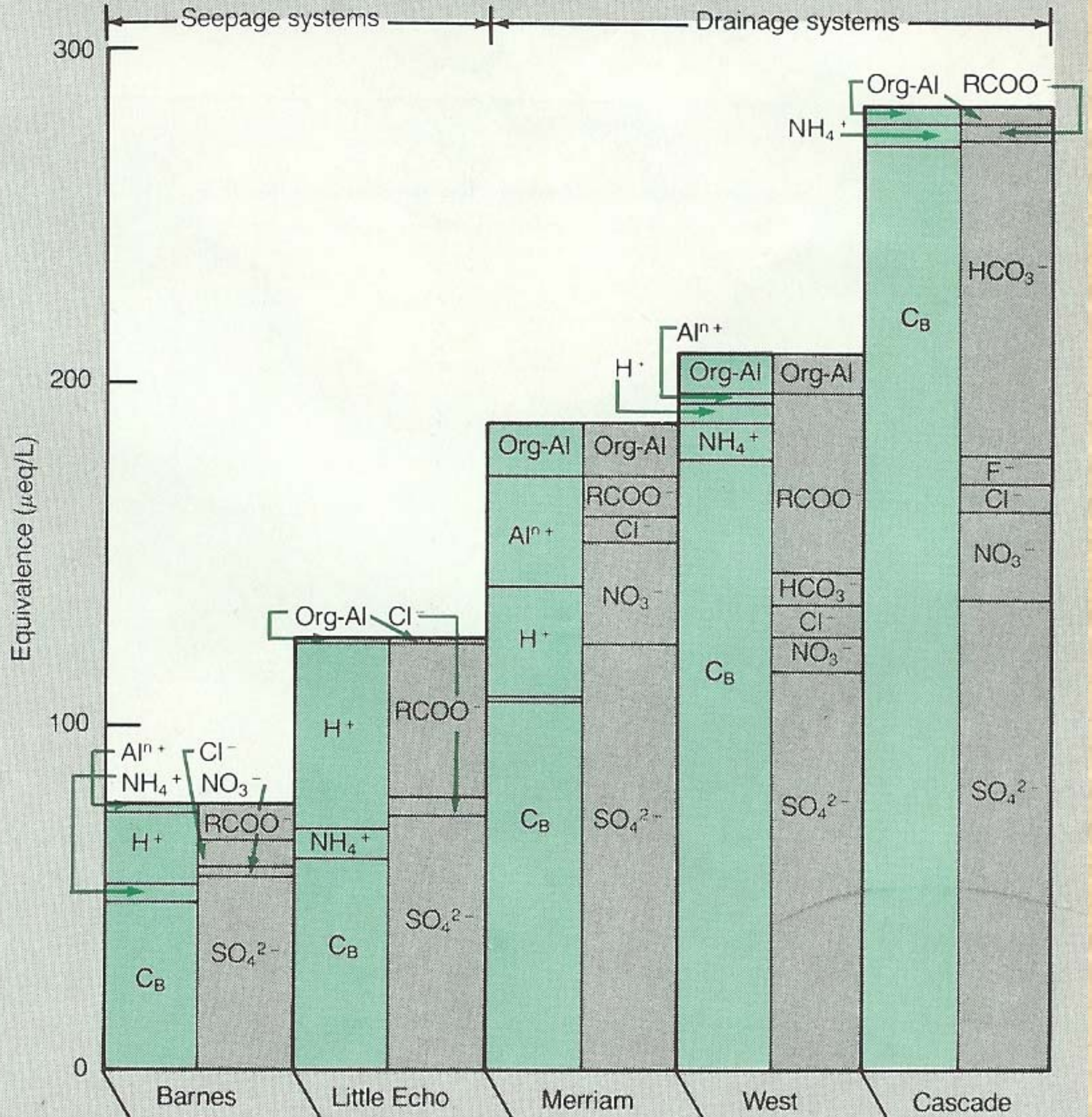


FIGURE 1

Adirondack lakes in the study[a]

[a] Sites not specifically indicated are located within the Big Moose system

Figure 2. Charge distribution in Adirondack lake waters



	Barnes	Little Echo	Merriam	West	Cascade
pH	4.7	4.3	4.5	5.3	6.6
DOC (μmol/L)	450	1100	480	670	310
H_4SiO_4 (μmol/L)	1	5	78	83	126

[a]Values represent 26-month averages

Barnes and Little Echo are clearwater and brownwater seepage ponds, respectively. Merriam, West, and Cascade are acidic, bog, and neutral pH drainage lakes, respectively

C_B is the sum of basic cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) equivalence

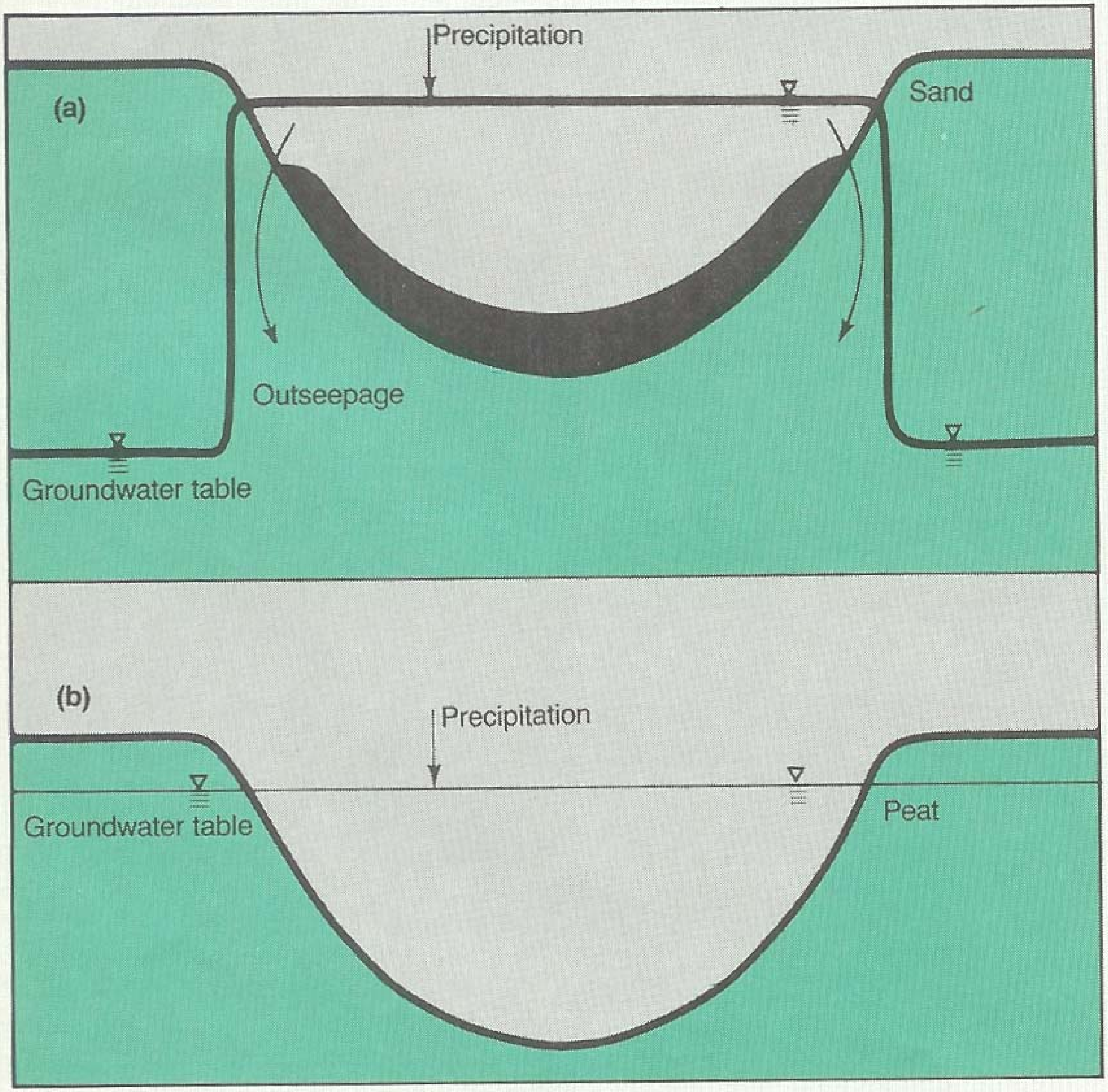
The equivalence of labile monomeric Al (Al^{n+}) is calculated by considering the various inorganic complexes

Nonlabile monomeric Al (Org-Al) is assumed to be trivalent and balanced by an equivalent organic ligand

Free organic anions are calculated as the difference between inorganic cations and inorganic anions

Driscoll and Newton, 1985

Figure 3: Acid-sensitive seepage lakes

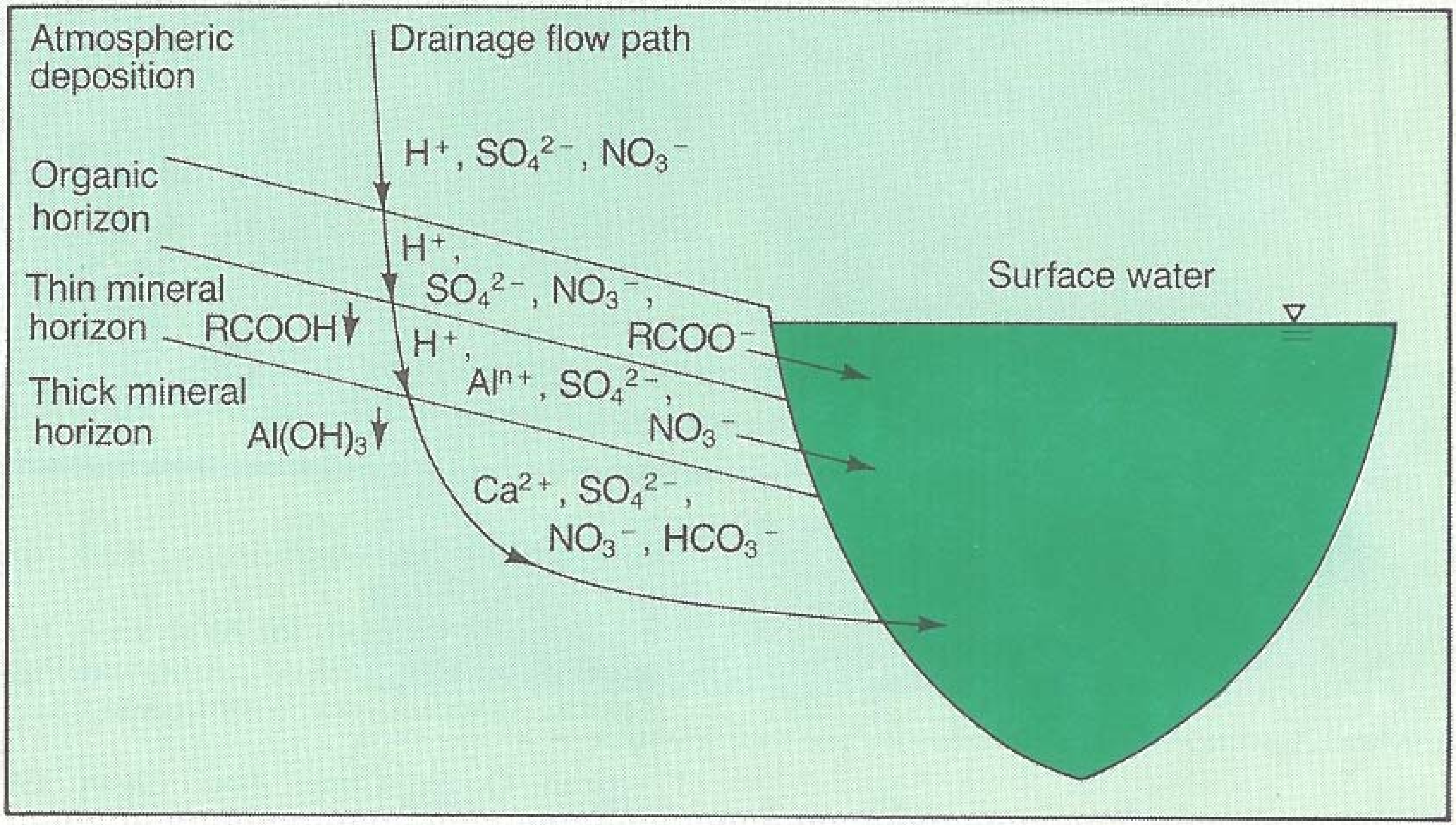


[a]Surface water in these lakes is isolated from the surrounding groundwater. In perched seepage lakes (a) the water is above the regional groundwater table because of the low permeability of organic rich bottom sediments. Bog seepage lakes (b) are surrounded by thick peat deposits that restrict significant movement of groundwater into the lake. Solute concentrations in isolated seepage lakes are strongly influenced by atmospheric deposition

Driscoll and Newton, 1985

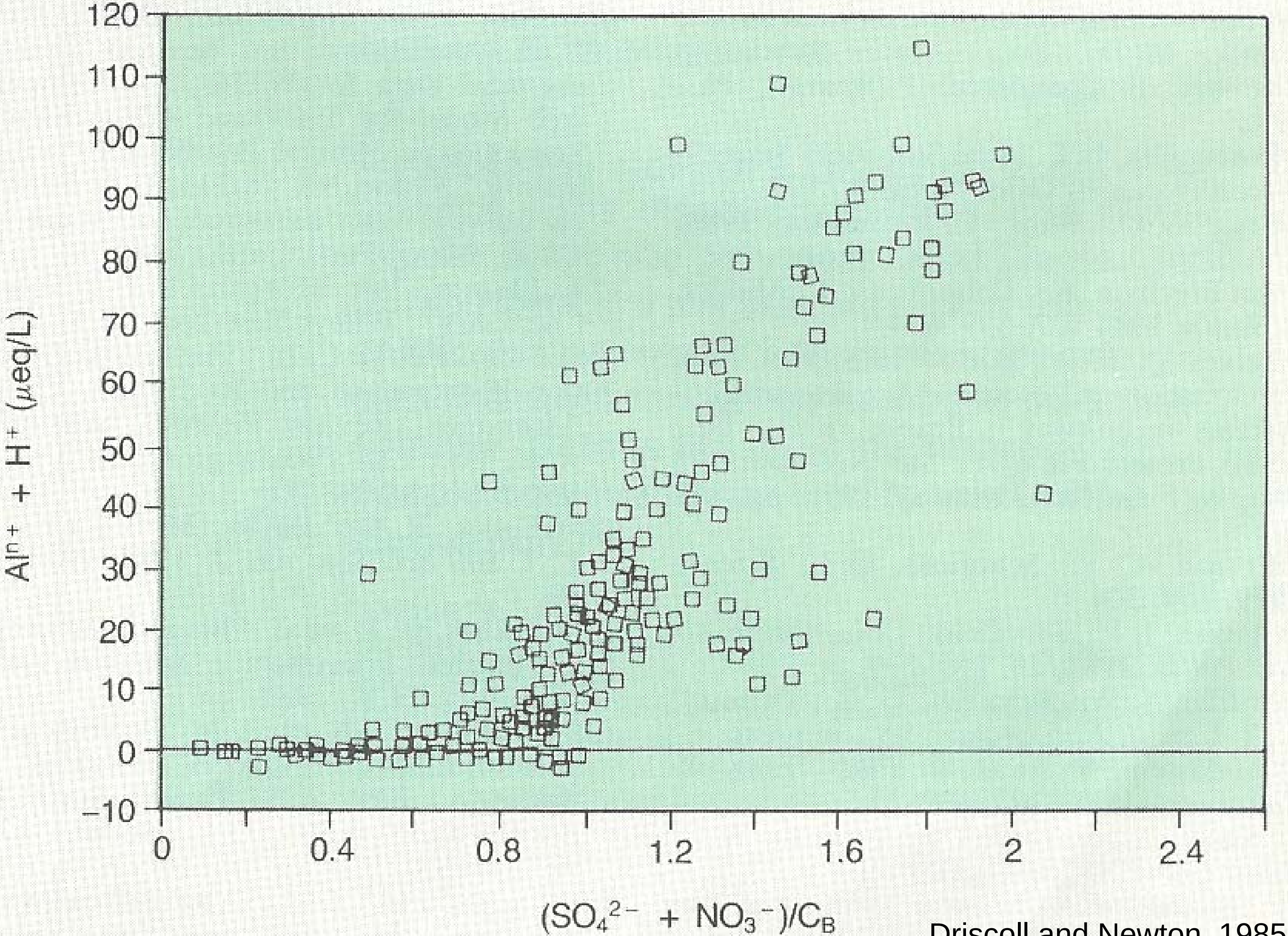
Figure 4: Chemical transformations associated with water flow paths to a drainage lake

Driscoll and Newton, 1985



As water containing acidic deposition migrates through organic soil and peat, the resulting solution will contain mineral and organic acids. Water moving through shallow acidic soil will deposit organic solutes and mineral acids will solubilize Al, causing a solution with concentration levels of H^+ and Al. If acidic solutions are transported through thick mineral soil, H^+ and Al will be neutralized by the release of basic cations

Figure 5. Equivalence of acidic cations



Driscoll and Newton, 1985

[a](Al^{n+}) as a function of the ratio of SO_4^{2-} and NO_3^- equivalence to basic cation (C_B) equivalence for the 20 lakes in the study

http://pubs.acs.org/cgi-bin/article.cgi/esthag/2003/37/i10/pdf/es020924h.pdf

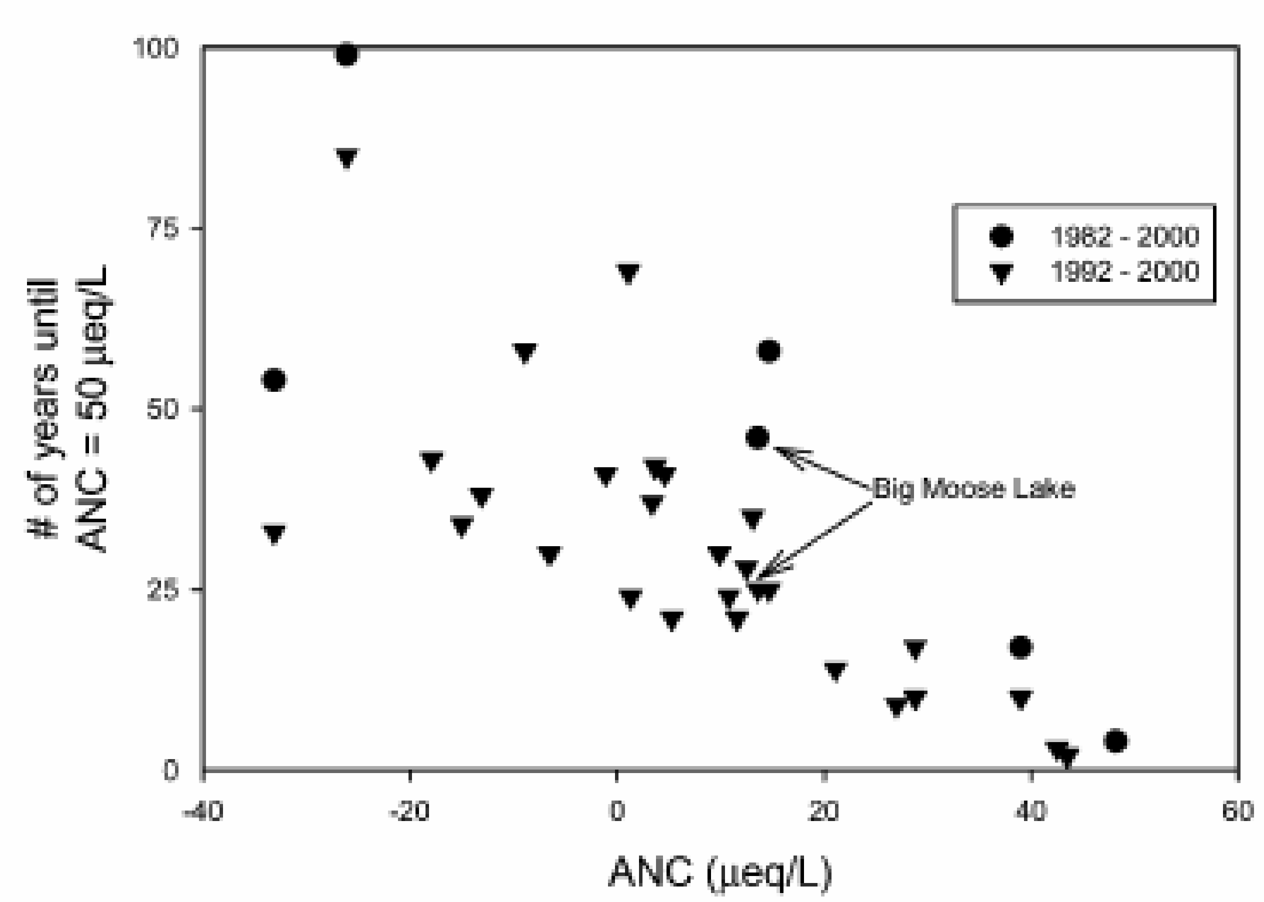


FIGURE 3. Time for lakes to reach acid-neutralizing capacity (ANC) values of 50 μequiv L^{-1} as a function of ANC value in the year 2000. These values are extrapolated assuming a linear rate of change based in slope of ANC change from time–series analysis. The extrapolation was done for two intervals, 1982–2000 and 1992–2000. Six lakes were evaluated for the longer record, and 28 lakes were evaluated for the shorter record. Note that rates of ANC increase were generally greater when calculated over the later interval, so the time to reach 50 μequiv L^{-1} is shorter. Lakes with $\geq$50 μequiv L^{-1} in 2000 or not showing a positive trend in ANC are not represented here.

Feasibility of liming the lakes?

ILWAS → an acid study.

Proposal: Liming the lakes with $CaCO_3$ and observe pH

- found that this effect didn't last very long although an initial rise in pH was observed.
- $CaCO_3$ quickly sinks to the bottom and becomes sediment.
- Also depends on the residence time of the lake (about 6 months to a year)
- Eventually controlling pH is not just acid input, but also depends on the size of the watershed and soil horizon, and the type of watershed, not just on what is in the lake.

Add lime to watershed directly?

- to effectively replace the Ca cations that were lost. Seems to make physical sense.
- But would it have much ecological damage?
- Wood's Lake area was limed two years ago and the ecological effects were checked.
- Fairly cost effective.

What happens if you stop inputting acid? Will the lake recover?

- No, not necessarily.
- Initially, the soil buffers to keep the acid from being a problem.
- But once the system is depleted of cations and Al is in their place, now the system is saturated with Al and it will take a very long time for the system to "wash out." Plus, where are you getting the new cations? Takes 1000's of years to develop a soil profile.

Ion exchange: delays acid input (Al→Ca) but once there, is there for a long time.

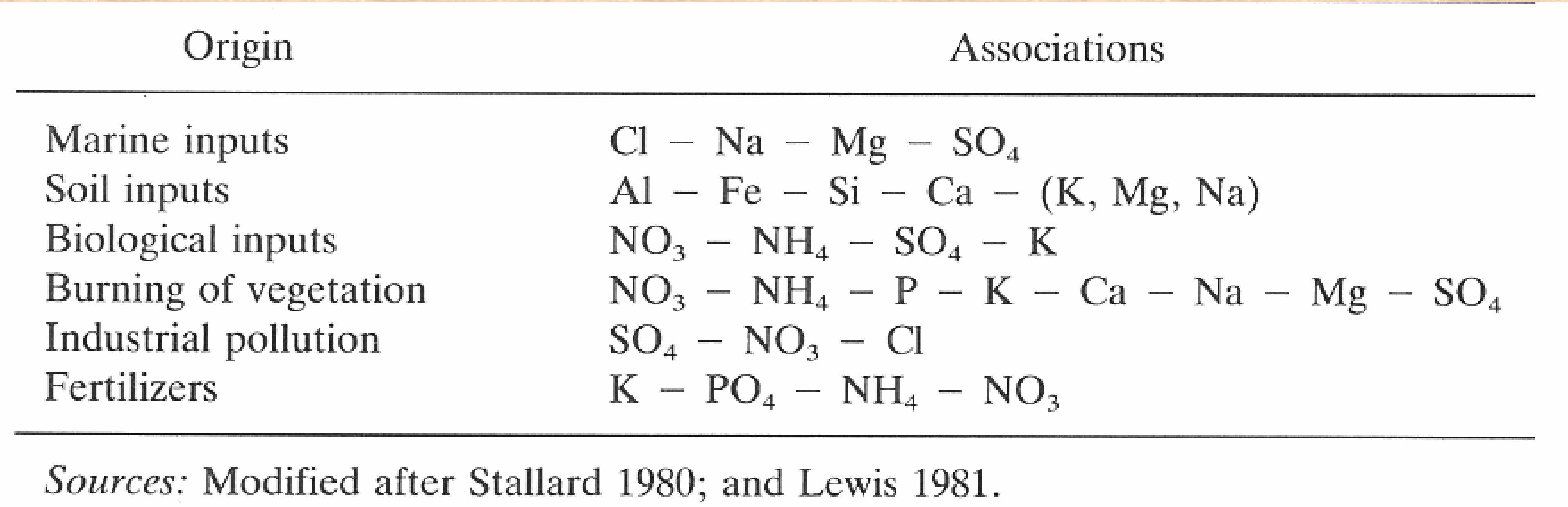
- If acid inputs were stopped now, things would probably not go back to normal but would maintain status quo.

Also happens with radioactive materials

- 137Cs and 90Sr → both quite high and bad from the nuclear testing days. Sr is a large molecule and through an inorganic exchange will adsorb onto molecules.
  - Sr moves 30 x slower than water itself through the soil.

  → Therefore it delays associated problems, but once there, will have problems for a very long time!

Primary Associations in Rain

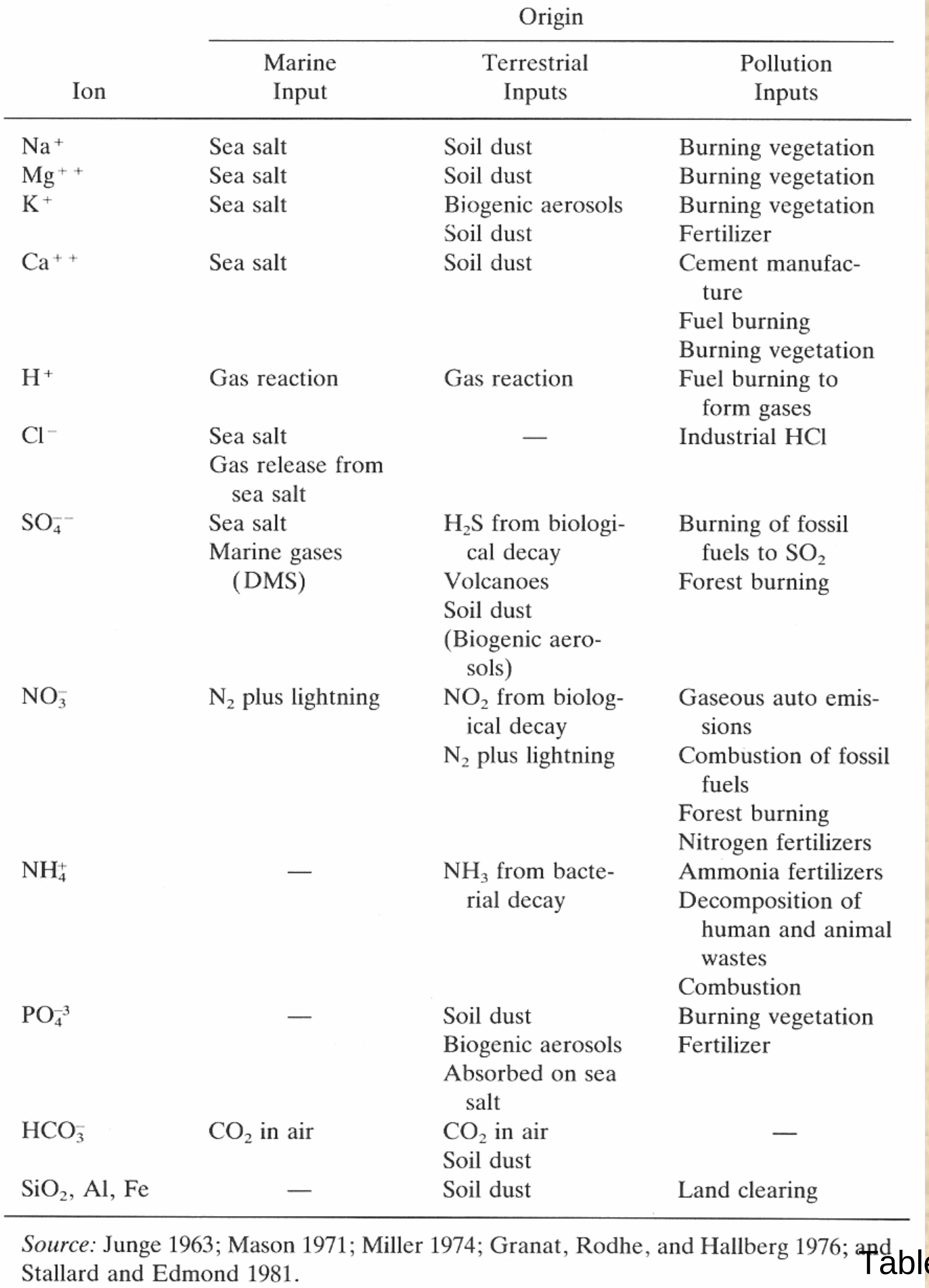


Origin	Associations
Marine inputs	$Cl - Na - Mg - SO_4$
Soil inputs	$Al - Fe - Si - Ca - (K, Mg, Na)$
Biological inputs	$NO_3 - NH_4 - SO_4 - K$
Burning of vegetation	$NO_3 - NH_4 - P - K - Ca - Na - Mg - SO_4$
Industrial pollution	$SO_4 - NO_3 - Cl$
Fertilizers	$K - PO_4 - NH_4 - NO_3$

Sources: Modified after Stallard 1980; and Lewis 1981.

Table 3.3. Berner. *The Global Water Cycle*, 1987.

Sources of Individual Ions in Rainwater



	Origin		
Ion	Marine Input	Terrestrial Inputs	Pollution Inputs
Na^+	Sea salt	Soil dust	Burning vegetation
Mg^{++}	Sea salt	Soil dust	Burning vegetation
K^+	Sea salt	Biogenic aerosols Soil dust	Burning vegetation Fertilizer
Ca^{++}	Sea salt	Soil dust	Cement manufacture Fuel burning Burning vegetation
H^+	Gas reaction	Gas reaction	Fuel burning to form gases
Cl^-	Sea salt Gas release from sea salt	—	Industrial HCl
SO_4^{--}	Sea salt Marine gases (DMS)	H_2S from biological decay Volcanoes Soil dust (Biogenic aerosols)	Burning of fossil fuels to SO_2 Forest burning
NO_3^-	N_2 plus lightning	NO_2 from biological decay N_2 plus lightning	Gaseous auto emissions Combustion of fossil fuels Forest burning Nitrogen fertilizers
NH_4^+	—	NH_3 from bacterial decay	Ammonia fertilizers Decomposition of human and animal wastes Combustion
PO_4^{-3}	—	Soil dust Biogenic aerosols Absorbed on sea salt	Burning vegetation Fertilizer
HCO_3^-	CO_2 in air	CO_2 in air Soil dust	—
SiO_2, Al, Fe	—	Soil dust	Land clearing

Source: Junge 1963; Mason 1971; Miller 1974; Granat, Rodhe, and Hallberg 1976; and Stallard and Edmond 1981.

Table 3.4. Berner. *The Global Water Cycle*, 1987.

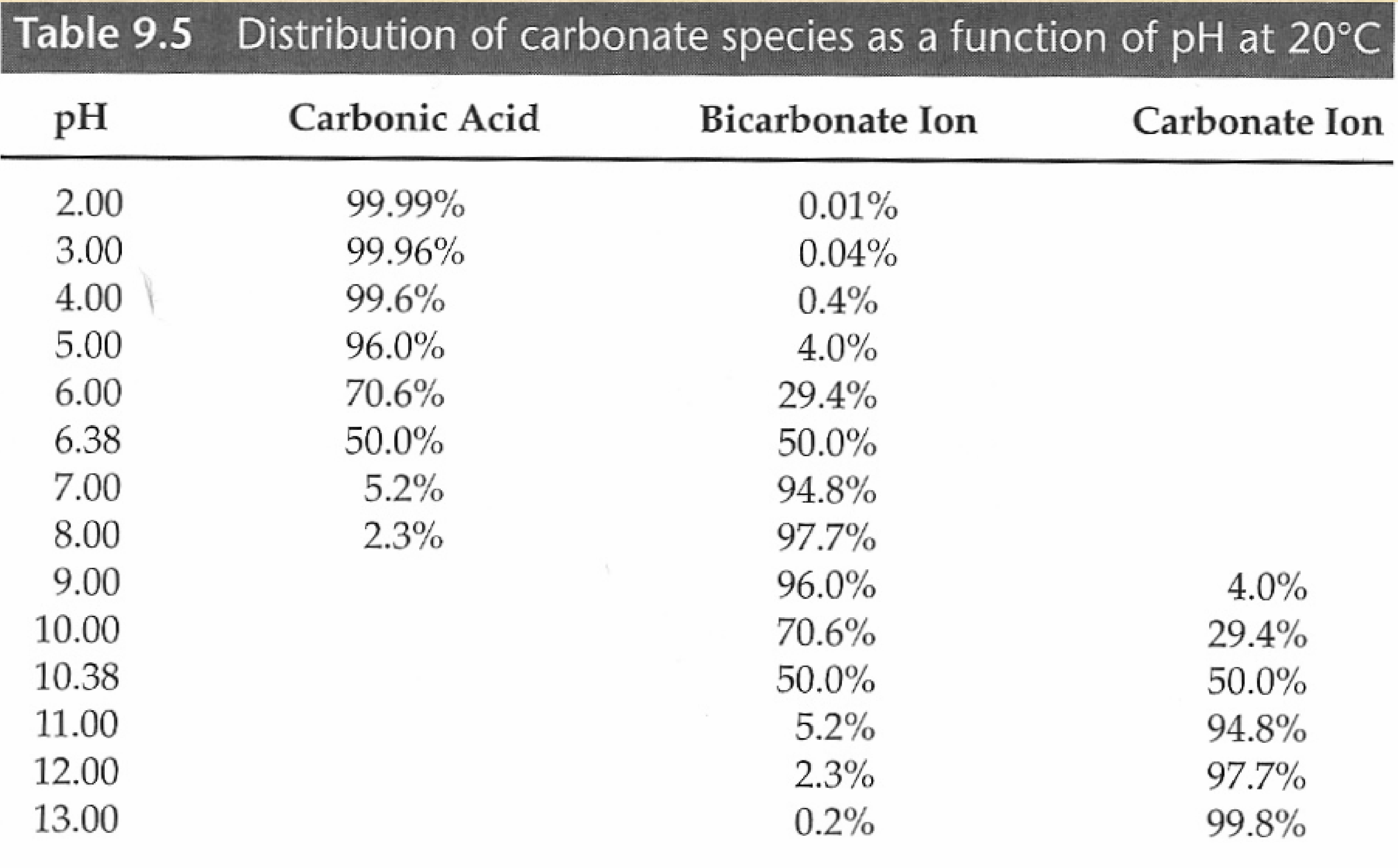
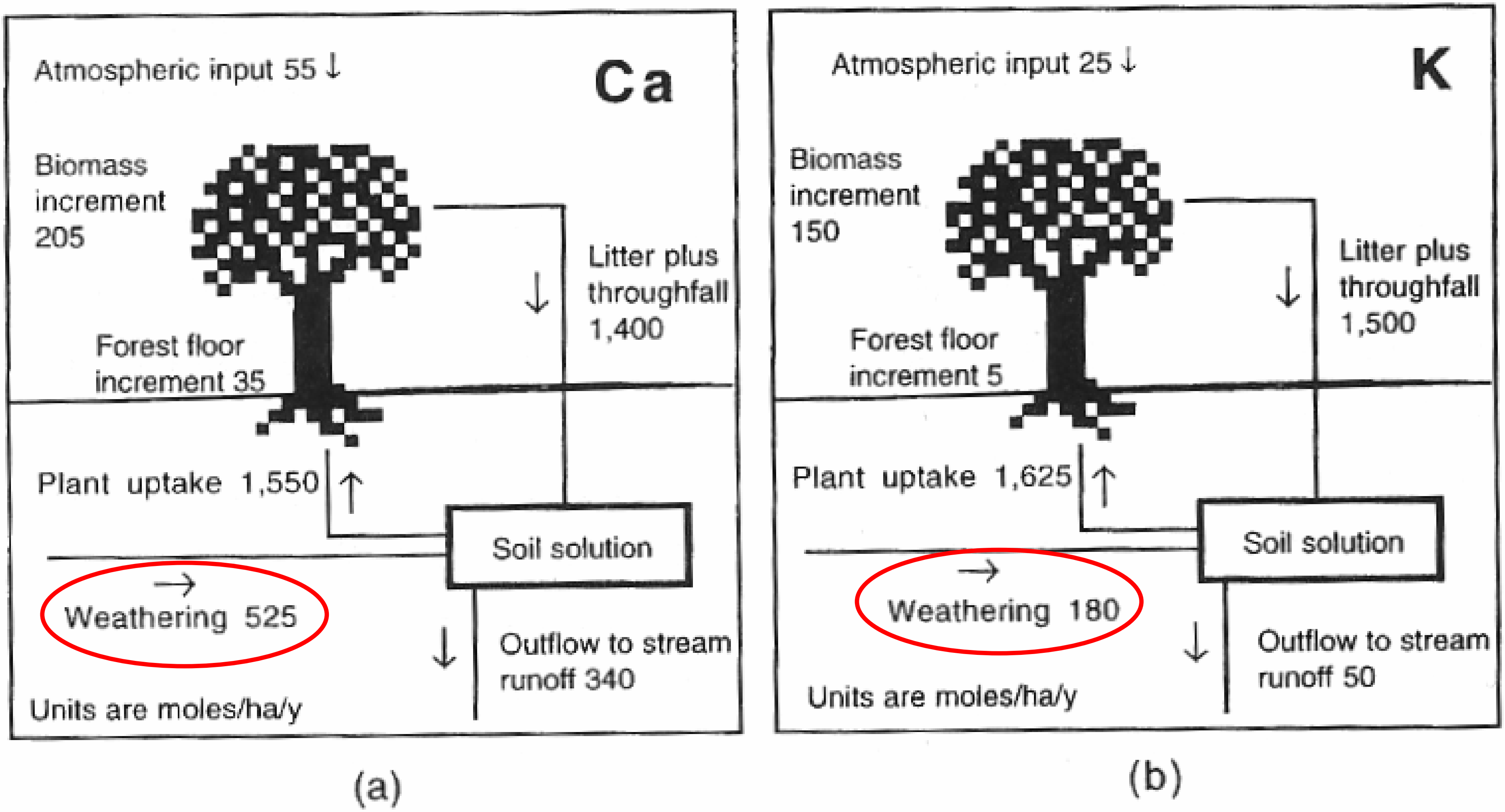


Table 9.5 Distribution of carbonate species as a function of pH at 20°C

pH	Carbonic Acid	Bicarbonate Ion	Carbonate Ion
2.00	99.99%	0.01%	
3.00	99.96%	0.04%	
4.00	99.6%	0.4%	
5.00	96.0%	4.0%	
6.00	70.6%	29.4%	
6.38	50.0%	50.0%	
7.00	5.2%	94.8%	
8.00	2.3%	97.7%	
9.00		96.0%	4.0%
10.00		70.6%	29.4%
10.38		50.0%	50.0%
11.00		5.2%	94.8%
12.00		2.3%	97.7%
13.00		0.2%	99.8%

Fetter, *Applied Hydrogeology 4th Edition*

Calcium and potassium fluxes at the Hubbard Brook Experimental Watershed



(a)

(b)

Figure 12-3 Drever, *The Geochemistry of Natural Waters*, 1997

- Why do people lime their soil?

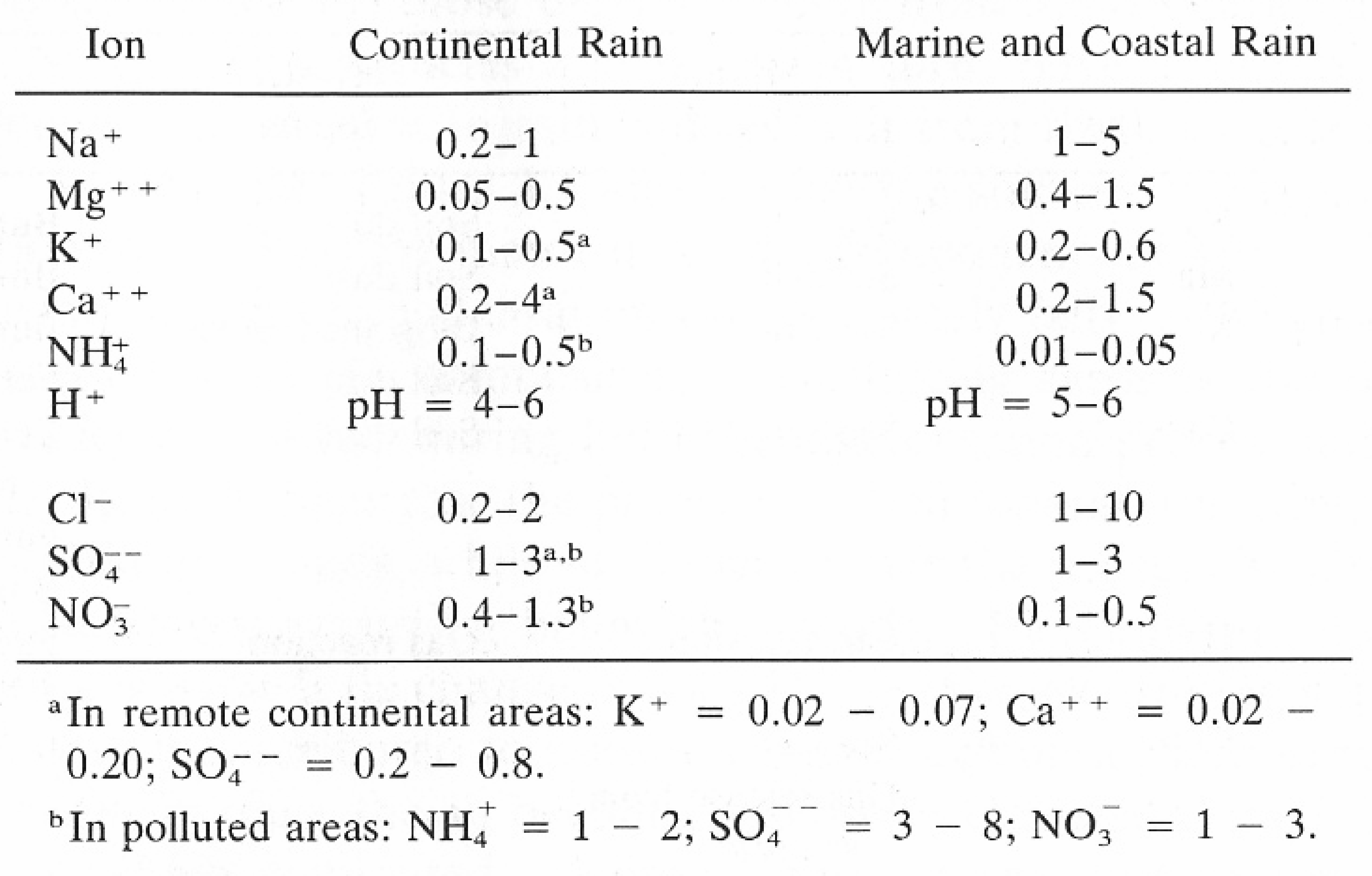
  In order to add back $CaCO_3$ or $(Ca,Mg)CO_3$ since the soil has become too acidic (which moss likes).

- Where does the Ca, Mg go?

  Trees use this as essential nutrients (Ca, K,) in through their root systems and excretes $2H^+$ → promotes acidity.

- In the long run, all the Ca and K in the leaves will fall to the ground and dissolve and put the Ca and K back into the soil again. But with farming, or raking, etc., this process is not allowed.

Typical Concentrations of Major Ions in Continental and Marine Rainfall (in mg/l)



Ion	Continental Rain	Marine and Coastal Rain
Na^+	0.2–1	1–5
Mg^{++}	0.05–0.5	0.4–1.5
K^+	0.1–0.5[a]	0.2–0.6
Ca^{++}	0.2–4[a]	0.2–1.5
NH_4^+	0.1–0.5[b]	0.01–0.05
H^+	pH = 4–6	pH = 5–6
Cl^-	0.2–2	1–10
SO_4^{--}	1–3[a,b]	1–3
NO_3^-	0.4–1.3[b]	0.1–0.5

[a] In remote continental areas: $K^+ = 0.02 - 0.07$; $Ca^{++} = 0.02 - 0.20$; $SO_4^{--} = 0.2 - 0.8$.

[b] In polluted areas: $NH_4^+ = 1 - 2$; $SO_4^{--} = 3 - 8$; $NO_3^- = 1 - 3$.

Table 3.5. Berner. *The Global Water Cycle*, 1987

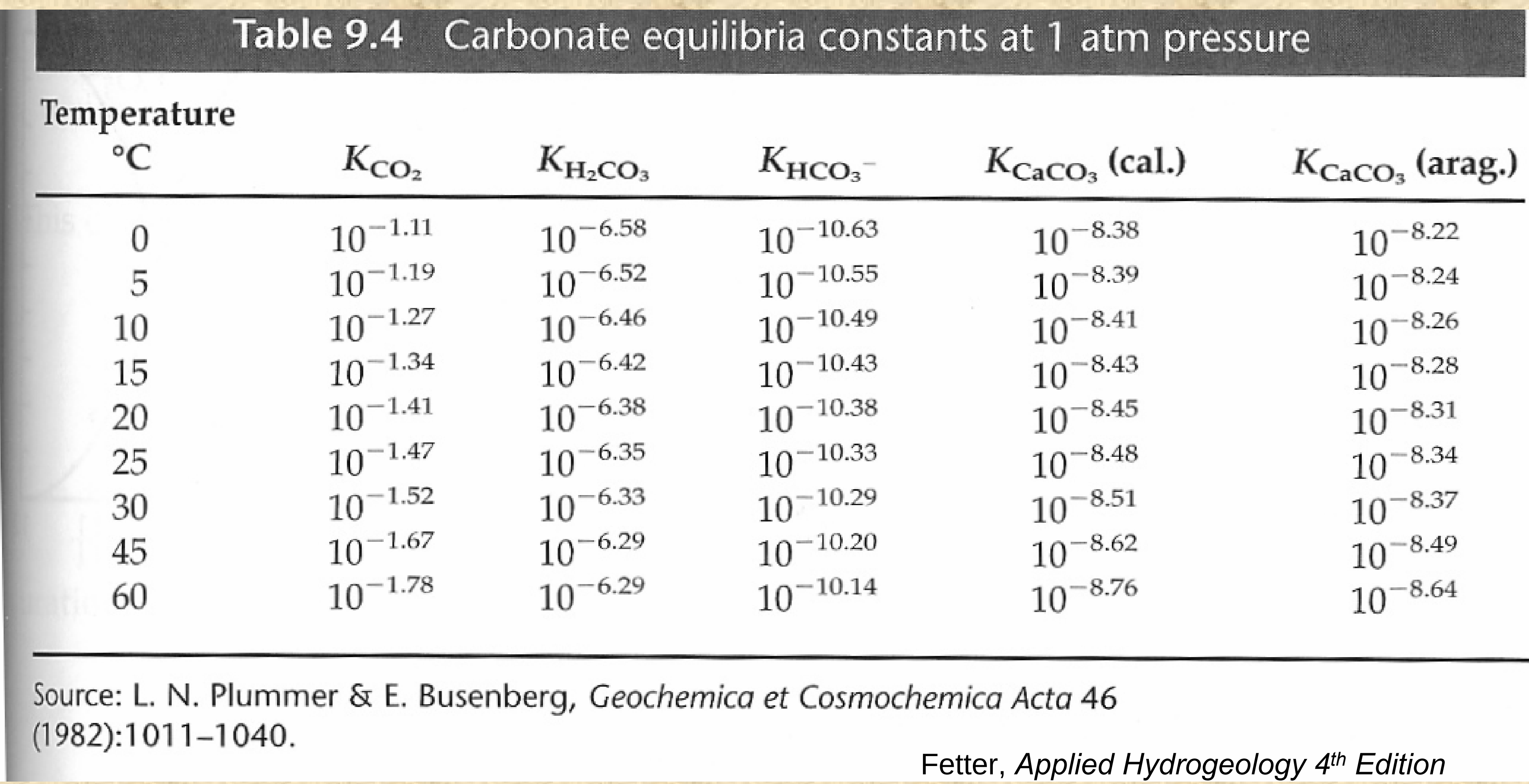


Table 9.4 Carbonate equilibria constants at 1 atm pressure

Temperature °C	K_{CO_2}	$K_{H_2CO_3}$	$K_{HCO_3^-}$	K_{CaCO_3} (cal.)	K_{CaCO_3} (arag.)
0	$10^{-1.11}$	$10^{-6.58}$	$10^{-10.63}$	$10^{-8.38}$	$10^{-8.22}$
5	$10^{-1.19}$	$10^{-6.52}$	$10^{-10.55}$	$10^{-8.39}$	$10^{-8.24}$
10	$10^{-1.27}$	$10^{-6.46}$	$10^{-10.49}$	$10^{-8.41}$	$10^{-8.26}$
15	$10^{-1.34}$	$10^{-6.42}$	$10^{-10.43}$	$10^{-8.43}$	$10^{-8.28}$
20	$10^{-1.41}$	$10^{-6.38}$	$10^{-10.38}$	$10^{-8.45}$	$10^{-8.31}$
25	$10^{-1.47}$	$10^{-6.35}$	$10^{-10.33}$	$10^{-8.48}$	$10^{-8.34}$
30	$10^{-1.52}$	$10^{-6.33}$	$10^{-10.29}$	$10^{-8.51}$	$10^{-8.37}$
45	$10^{-1.67}$	$10^{-6.29}$	$10^{-10.20}$	$10^{-8.62}$	$10^{-8.49}$
60	$10^{-1.78}$	$10^{-6.29}$	$10^{-10.14}$	$10^{-8.76}$	$10^{-8.64}$

Source: L. N. Plummer & E. Busenberg, *Geochemica et Cosmochemica Acta* 46 (1982):1011–1040.

Fetter, *Applied Hydrogeology 4th Edition*