Chemical Reactions!

Rearrangement of atoms and/or electrons to create new substances with different chemical and physical properties

Geochemical modeling

The practice of using thermodynamics and/or kinetics to analyze geochemical reactions that impact geologic systems

Recap

National Geographic

Recap

Congruent dissolution

- Dissolution of a mineral to produce only soluble species that are easily leached from soil
- Typical for salts, including carbonate and sulfate minerals
- Two-way street (minerals can re-precipitate under the right conditions)

Halite dissolution

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+ + Cl^-$$

Carbonate dissolution

$$CaCO_{3(s)} + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

Incongruent dissolution

- Dissolution of a mineral to produce solutes and one or more different mineral phases that remain in the soil
- Typical for silicate minerals; one-directional process

Albite ($NaAlSi_3O_8$) dissolution

$$NaAlSi_3O_{8\ (s)} + H_2O + CO_2 \rightarrow ???$$

Rule of thumb:

Silicate minerals + acidic water → base cations + alkalinity + silica + clay/oxide minerals

Precipitation Reaction

Evaporite deposits

Water removed through evaporation

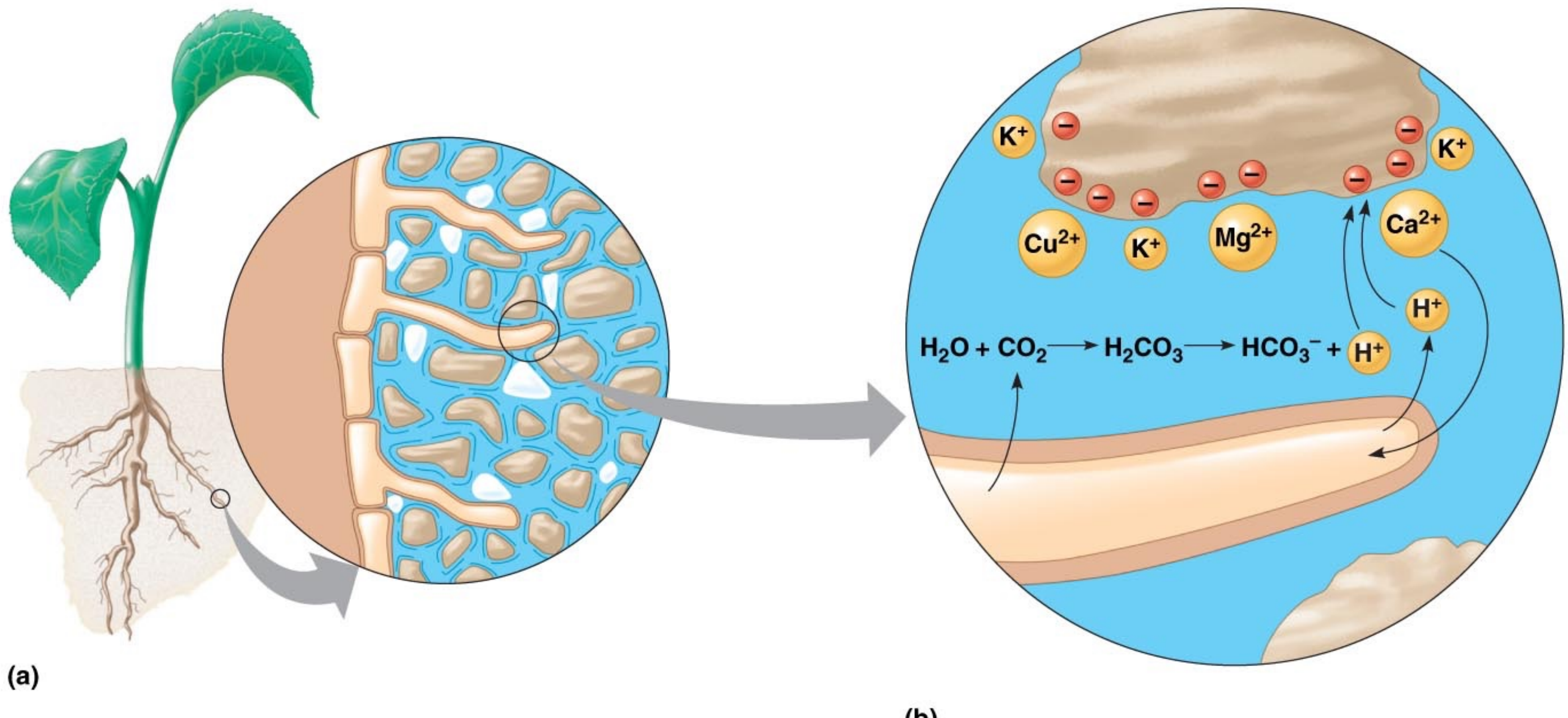
Pipe scaling

Recap

Acid-base reaction

Recap

Cation exchange in soils



Recap

Redox reaction in acid mine drainage

1) $FeS_2 + O_2 \rightarrow Fe^{2+} + SO_4^{2-} + H_2SO_4$
2) $Fe^{2+} + O_2 \rightarrow Fe^{3+}$
3) $Fe^{3+} + H_2O \rightarrow Fe(OH)_3$

What is oxidized and what is reduced in each reaction?

**unbalanced reactions

Recap

Lab 1 Paper Discussion
Chemical reactions in urban streams

Week	Date	Topic	Assignment Due	Reading
1	8/27	Lecture 1: Intro to Aqueous Geochemistry		
	8/29	Lecture 2: Chemistry and Chemical Reactions		Chapter 1
2	9/3	Lecture 3: Chemistry of Natural Waters		Chapter 2
	9/5	Lecture 4: Thermodynamics	Problem Set 1	Chapter 3
3	9/10	Lab 1	Lab 1 write-up	
	9/12	Lecture 5: Activity-Concentration Relationship		Chapter 4

Students must come to class prepared to discuss the assigned paper. Responses to paper discussions should be completed before class and turned in at the end of the class period on the day that the paper is discussed.

Chemistry of Natural Waters

- What is the approximate (inorganic) chemical composition of the major water reservoirs?

Topic outline

- Electroneutrality and charge balance
- Major dissolved chemicals (solutes) in waters
- Natural and anthropogenic sources of solutes to surface waters
- Composition of different water bodies
- Visualizing water chemistry

Electroneutrality and charge balance

- The sum of charges on all ions in water must equal zero
- Calculated using *equivalent* concentration, where **equivalent (eq/L) = molar concentration of ion (mol/L) × charge of the ion**

What are the concentrations of Ca^{2+} and Cl^{-} in meq/L for a 10 mmol/L $CaCl_2$ solution?

Refer to the note

Recap

Is Lake Harriet (Minneapolis) charge balanced?

Major inorganic solutes:

Cation concentrations (mg/L)			Anion concentrations (mg/L)		
	mg/L	meq/L		mg/L	meq/L
Ca^{2+}	40		HCO_3^-	131	
Mg^{2+}	13		SO_4^{2-}	9	
Na^+	50		Cl^-	97	
K^+	5.6		NO_3^-	0.04	
Cation sum			**Anion sum**		

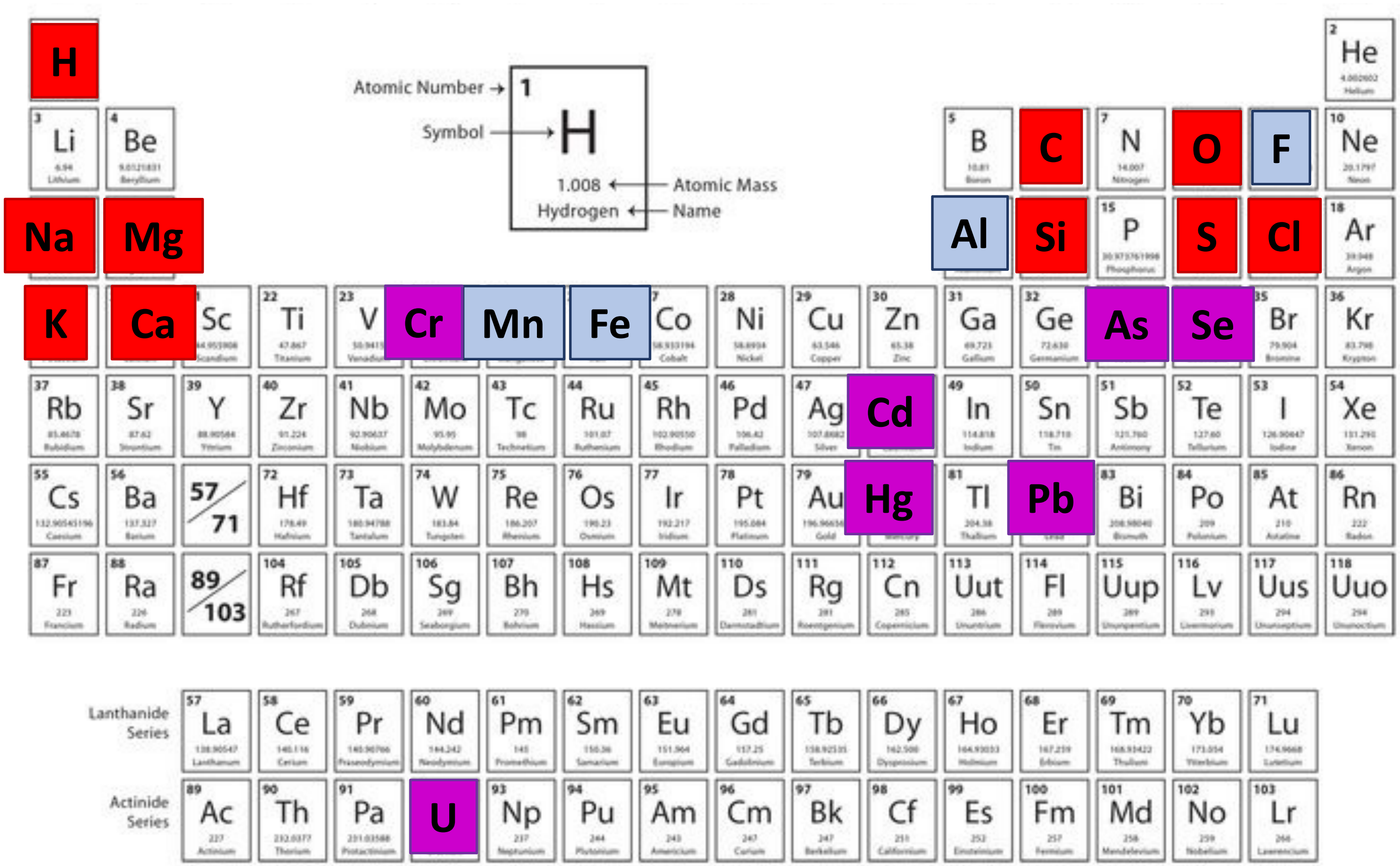
Is Lake Harriet (Minneapolis) charge balanced?

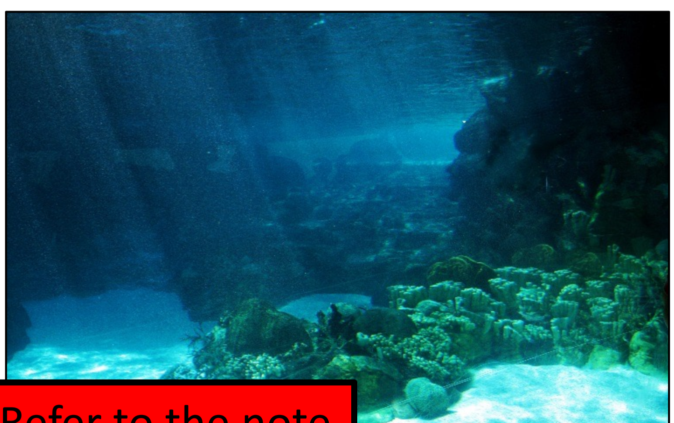
Major inorganic solutes:

Cation concentrations (mg/L)			Anion concentrations (mg/L)		
	mg/L	meq/L		mg/L	meq/L
Ca^{2+}	40	2.00	HCO_3^-	131	2.15
Mg^{2+}	13	1.07	SO_4^{2-}	9	0.09
Na^+	50	2.17	Cl^-	97	2.74
K^+	5.6	0.14	NO_3^-	0.04	0.0006
Cation sum			**Anion sum**		

Important chemical species in natural waters

Major elements: H, C, O, Na, Mg, Si, S, Cl, K, Ca
Minor elements: F, Al, Mn, Fe
Trace elements: Li, B, Ti, V, Cr, Co, Ni, Cu, Zn, Br, Sr, Mo, Ag, I, Au
Trace pollutants: Cr, As, Se, Cd, Hg, Pb, U, etc.
Major nutrients: C, H, N, O, P, S (comprise majority of all living organisms)

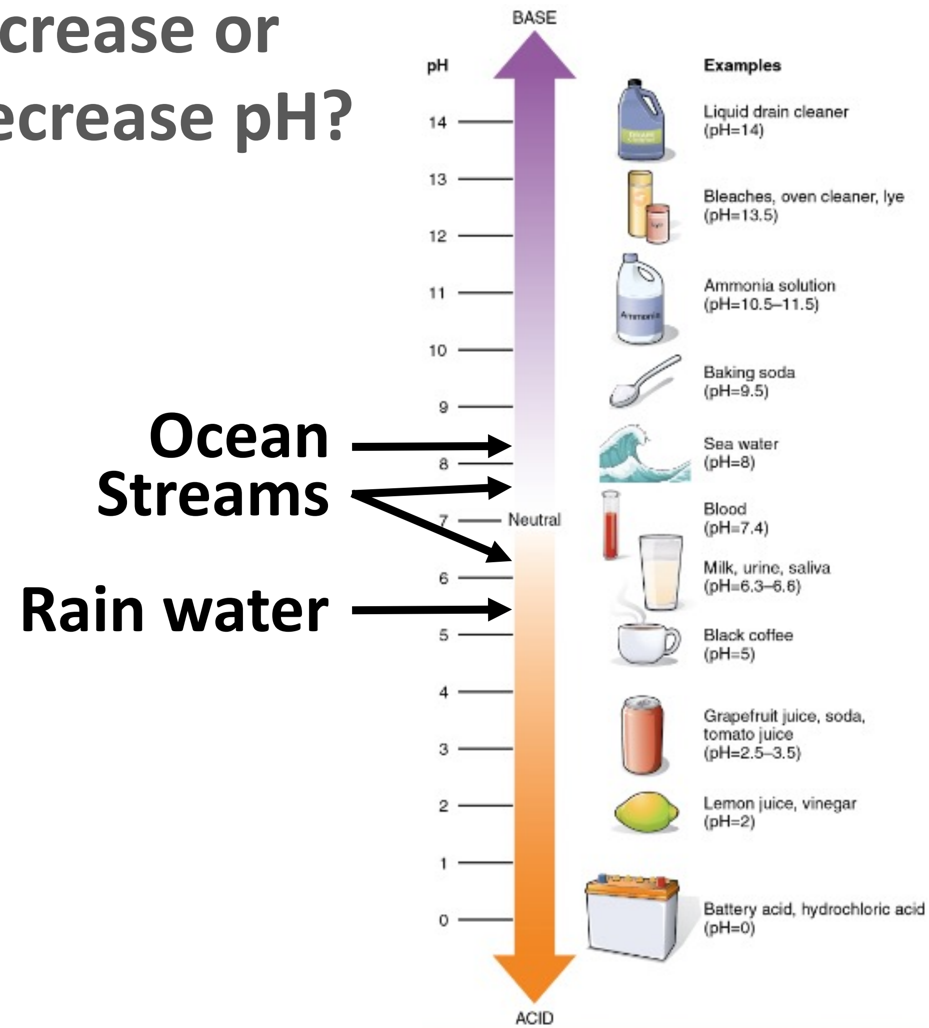


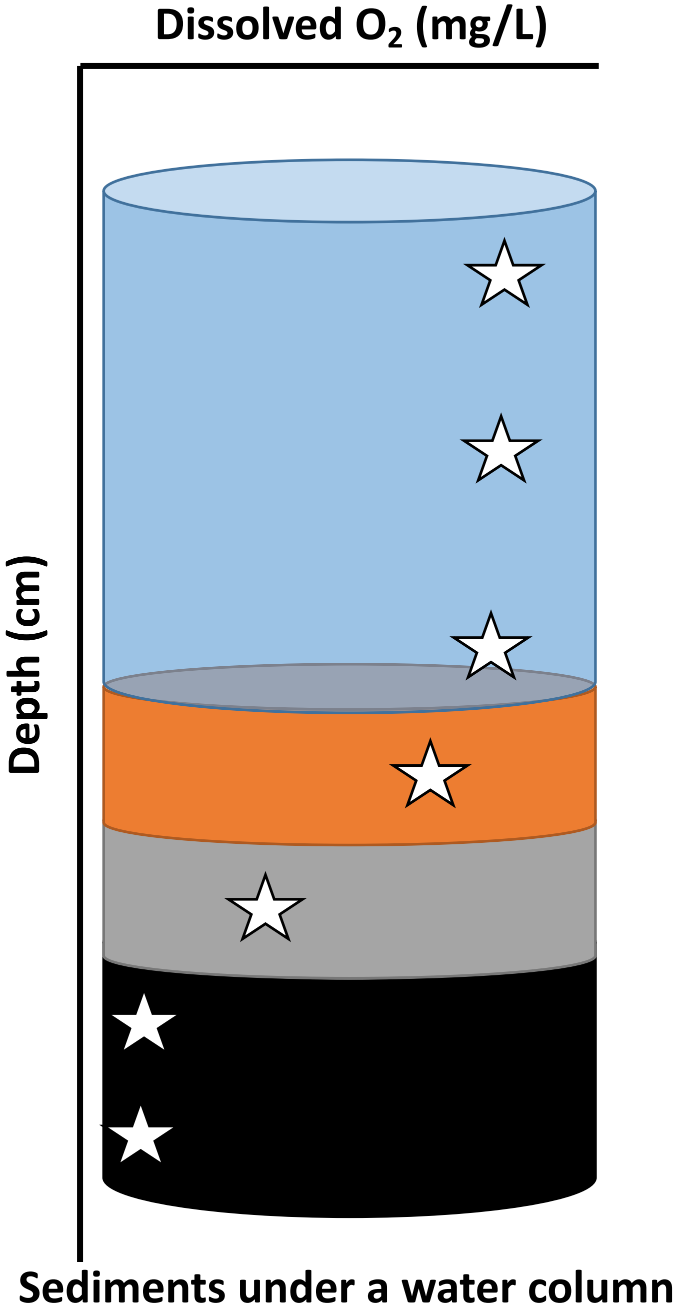


Refer to the note

pH of Natural Waters

- pH generally increases as water travels through the landscape
- What factors increase or decrease pH?





Refer to the note

Redox conditions are determined by the relative abundance of of e- donors and acceptors

- **Driven by O_2 gas availability**

- **Oxic –** O_2 gas present
  - "oxidizing" environment
- **Suboxic –** low O_2 gas present; respiration with O_2 is hindered
- **Anoxic –** no O_2 present; organisms "breathe" other chemicals
  - "reducing" environment

The Big Eight

- **These species make up 95-99% of all inorganic solutes in natural waters**
- **Why? – abundant in the Earth's crust and generally soluble in water**

CATIONS	ANIONS	UNCHARGED
Ca^{2+}	HCO_3^-	$Si(OH)_4^0$
Mg^{2+}	SO_4^{2-}	
Na^+	Cl^-	
K^+		

Minor solutes of utmost importance: Al, Fe, Mn

Base Cations

- **Na^+, K^+, Ca^{2+}, Mg^{2+}**
- Do not participate in redox reactions; limited acid-base reactions
- Particularly dominant cations in ***basic*** environments
- Rock-derived

Bicarbonate anion

- **HCO_3^-**
- important acid-base chemistry (readily gives and receives protons)
- major component of *alkalinity* (acid-neutralizing capacity of waters)
- Atmospheric and rock-derived

$$\underset{\text{carbon dioxide}}{CO_2} + \overset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3} \rightleftharpoons \overset{\text{hydrogen ion}}{H^+} + \underset{\text{bicarbonate ion}}{HCO_3^-} \rightleftharpoons \overset{\text{hydrogen ion}}{H^+} + \underset{\text{carbonate ion}}{CO_3^{2-}}$$

Sulfate anion

- **SO_4^{2-}**
- undergoes redox reactions to form different sulfur species (e.g., H_2S)
- Rock-derived; atmospheric inputs are important

Chloride anion

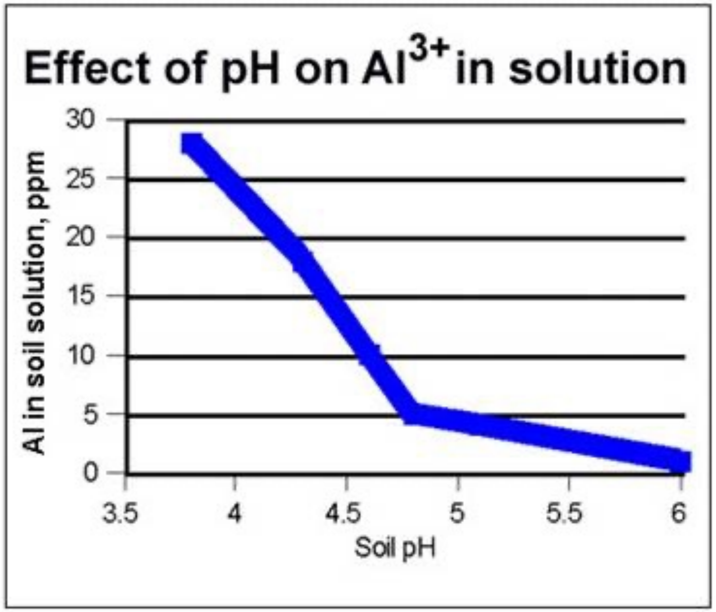
- **Cl^-**
- Non-reactive in the environment, hence a “conservative” ion
- Mostly input to surface waters from precipitation

Dissolved silica (aka silicic acid)

- **$Si(OH)_4^0$**
- the silica tetrahedron that is released during weathering of silicate rocks (rock-derived)
- Uncharged species (not an ion)

Aluminum (Al) – exists in water as Al^{3+}

- Not redox active
- Becomes soluble at low pH (< 5)
- Precipitates as mineral gibbsite, $Al(OH)_3$, above this pH



Al toxicity common in plants grown in acidic soils

Iron – exists in water as Fe^{2+} or Fe^{3+}

- redox-active (can gain/lose electrons)
- typically only soluble under acidic and/or anoxic conditions
- Fe^{3+} readily combines with water to form ferrihydrite precipitates

Acid mine drainage (AMD)

1) Fe^{2+} is released from pyrite (FeS_2) during weathering (exposure to oxygen and water)

2) Fe^{2+} reacts with O_2

$$Fe^{2+} + O_2 \rightarrow Fe^{3+}$$

3) Fe^{3+} is insoluble and precipitates

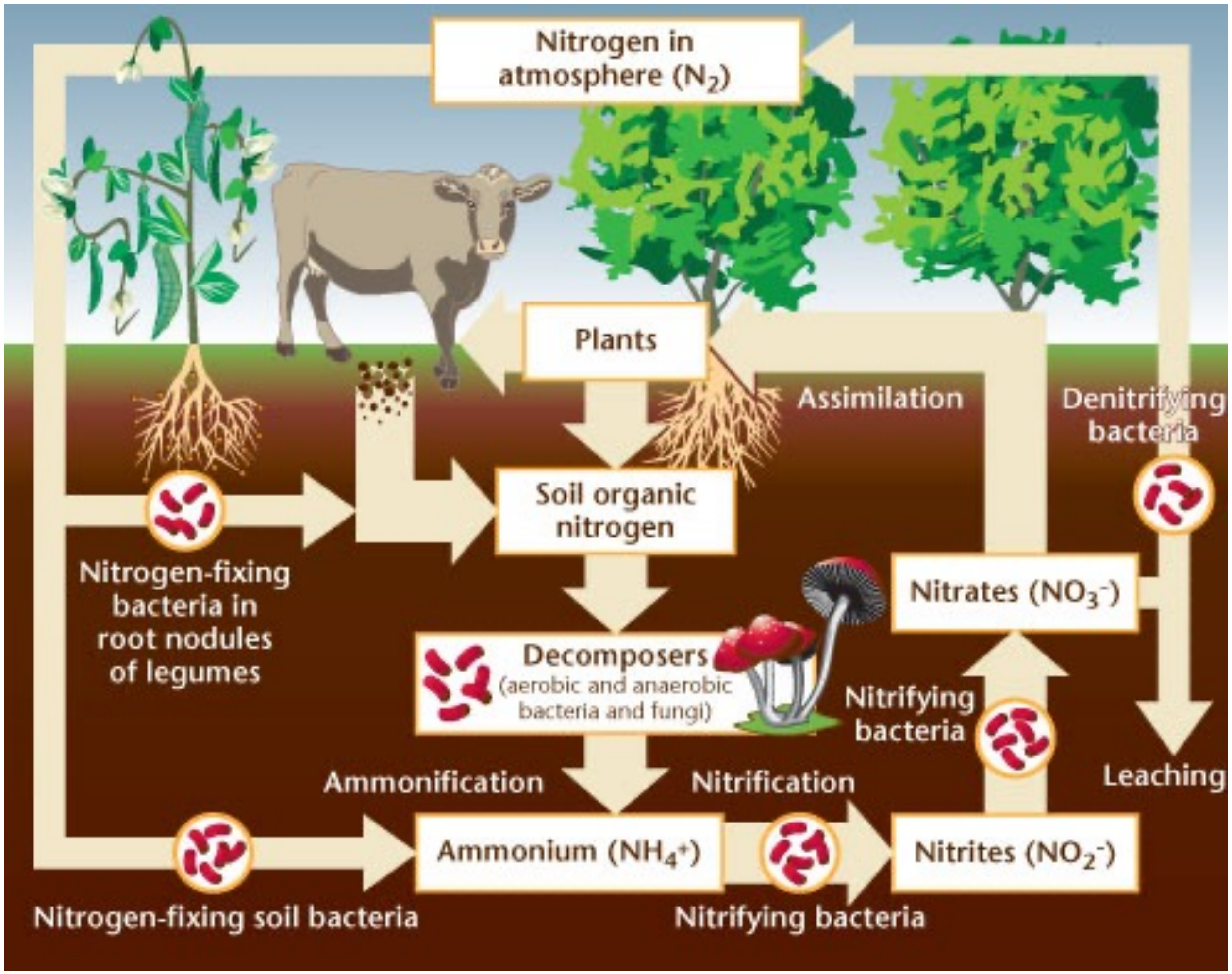
$$Fe^{3+} + H_2O \rightarrow Fe(OH)_3$$

Manganese - exists in water primarily as Mn^{2+}

- redox-active (can gain/lose electrons)
- becomes soluble under acidic and/or reducing conditions
- Insoluble under oxic conditions, but Mn^{2+} oxidation is very slow (kinetically limited)
- Microorganisms (bacteria and fungi) catalyze Mn oxidation to form Mn-oxide minerals

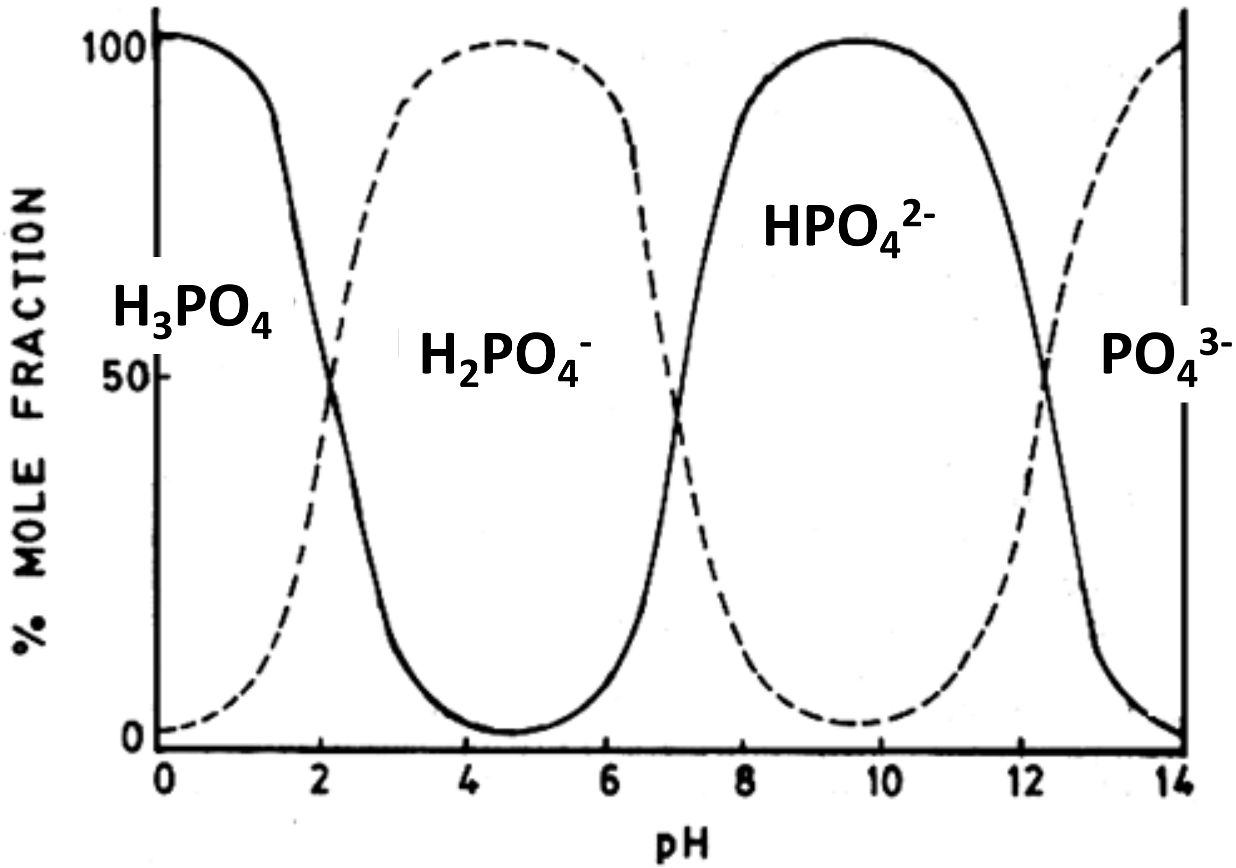
Nitrogen

- Input to soils via fixation from atmosphere and fertilizer
- Redox-active; present as ammonium cation (NH_4^+) and nitrate anion (NO_3^-)
- Lost from soils via leaching, plant harvest, denitrification



Phosphorus

- Input to soils via weathering of primary minerals and fertilizers
- Not redox-active; Soluble form is phosphate, PO_4^{3-}, which can acquire up to 3 H^+ under different pH conditions



What else is dissolved in water?

1) Dissolved organic matter (DOM)

- Dissolved organic carbon (DOC) – the fraction of DOM consisting of C

2) Dissolved gases

- O_2 (DO = dissolved oxygen), N_2, CO_2, CH_4

3) Nutrient ions

- NH_4^+ and NH_3 (ammonium and ammonia)
- NO_3^- and NO_2^- (nitrate and nitrite)
- Inorganic phosphorus (phosphate)
- Organic N and organic P

Sources of major and minor solutes

Natural sources

- Atmospheric
- Rock-derived (terrestrial)

Anthropogenic sources

- Most are ultimately derived from mineral resources, but present in high concentration at the Earth's surface due to extraction and processing
- What are sources of various solutes?

Online databases for water chemistry

USGS National Water Information System
http://waterdata.usgs.gov/nwis

STORET: water quality data related to pollution (EPA)
https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange

Water Quality Portal
http://waterqualitydata.us/

National Atmospheric Deposition Program
https://nadp.slh.wisc.edu

HydroClient (CUAHSI)
http://data.cuahsi.org/