

Chemical Reactions!

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

Geochemical modeling

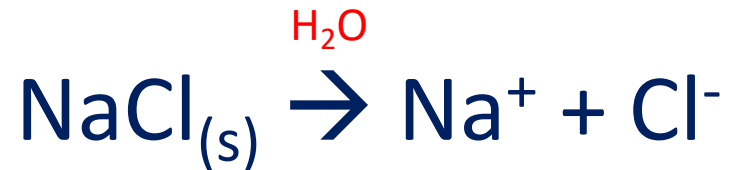
The practice of using thermodynamics and/or kinetics to analyze geochemical reactions that impact geologic systems



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



Carbonate dissolution



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 (NaAlSi₃O₈) dissolution



Rule of thumb:

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

Precipitation Reaction

Evaporite deposits

Water removed through evaporation



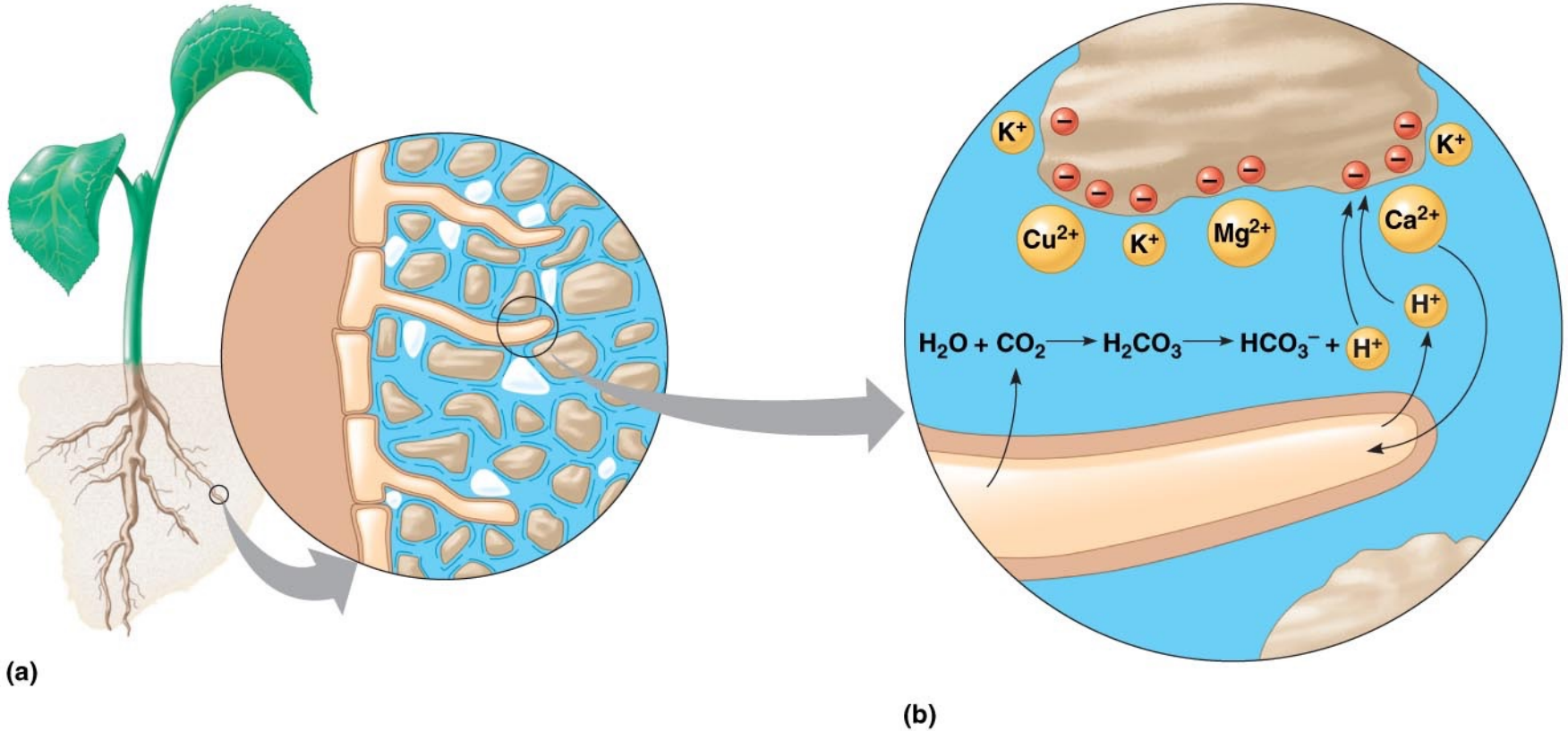
Pipe scaling

Recap

Acid-base reaction

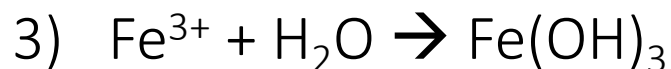
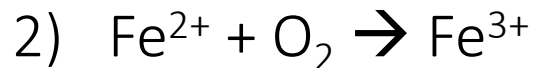
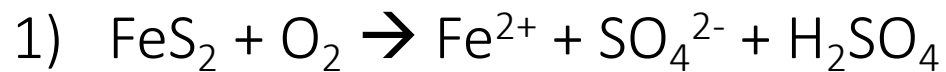


Cation exchange in soils



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Redox reaction in acid mine drainage



What is oxidized and what is reduced in each reaction?

**unbalanced reactions



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?



Temperance River, Tofte MN

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?

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

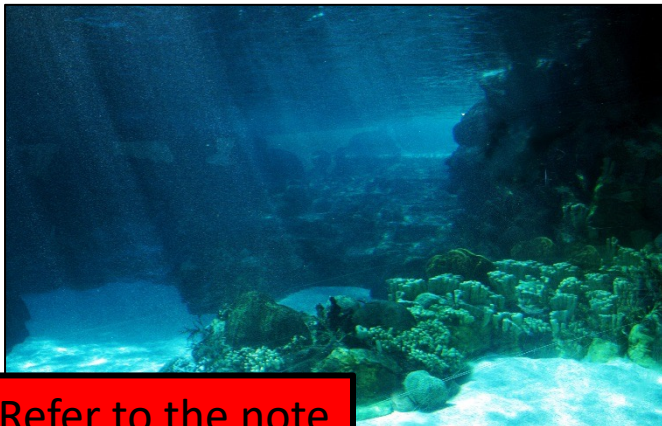
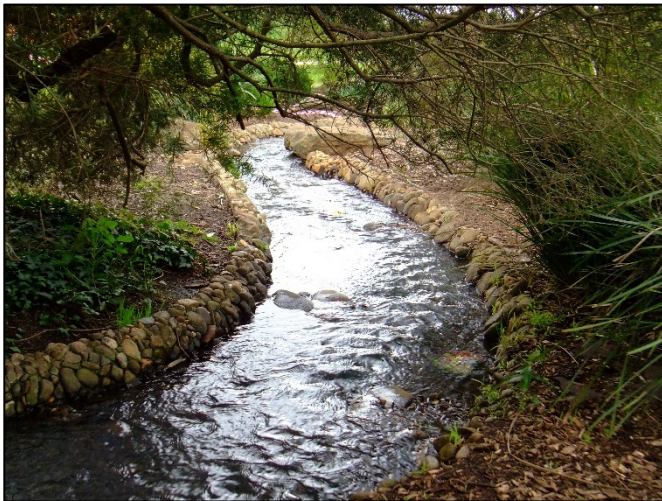
Minor elements: F, Al, Mn, Fe

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)

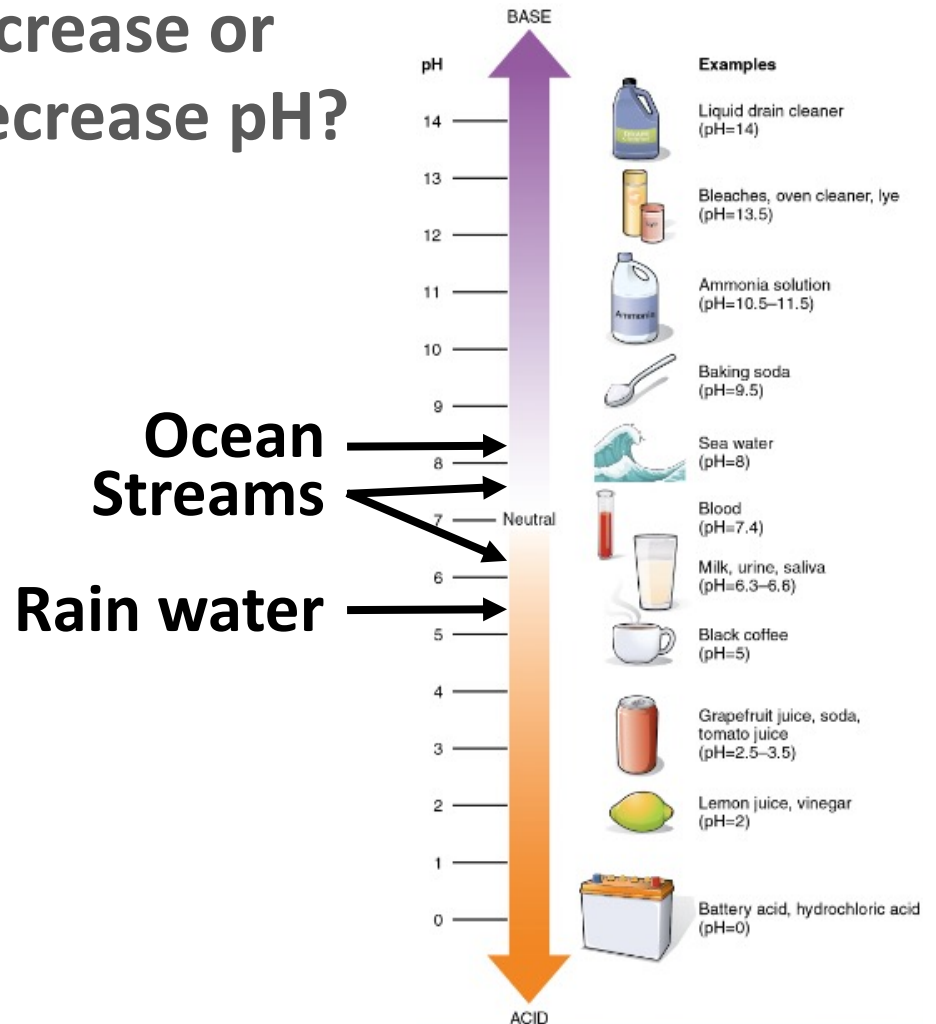
<div>Atomic Number → 1</div> <div>Symbol → H</div> <div>1.008 ← Atomic Mass</div> <div>Hydrogen ← Name</div>																										2 He 4.002602 Helium
3 Li 6.94 Lithium	4 Be 9.0121831 Beryllium															5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998 Fluorine	10 Ne 20.1797 Neon					
11 Na 22.990 Sodium	12 Mg 24.305 Magnesium															13 Al 26.982 Aluminum	14 Si 28.086 Silicon	15 P 30.974 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon					
19 K 39.098 Potassium	20 Ca 40.078 Calcium	21 Sc 44.956 Scandium	22 Ti 47.88 Titanium	23 V 50.942 Vanadium	24 Cr 51.996 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.933 Cobalt	28 Ni 58.693 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.922 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.796 Krypton									
37 Rb 85.468 Rubidium	38 Sr 87.62 Strontium	39 Y 88.906 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.906 Niobium	42 Mo 95.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.905 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.868 Silver	48 Cd 112.411 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.905 Iodine	54 Xe 131.29 Xenon									
55 Cs 132.905 Cesium	56 Ba 137.327 Barium	57 La 138.905 Lanthanum	71 Hf 178.49 Hafnium	72 Ta 180.948 Tantalum	73 W 183.84 Tungsten	74 Re 186.207 Rhenium	75 Os 190.23 Osmium	76 Ir 192.225 Iridium	77 Pt 195.084 Platinum	78 Au 196.967 Gold	79 Hg 200.59 Mercury	80 Tl 204.38 Thallium	81 Pb 207.2 Lead	82 Bi 208.980 Bismuth	83 Po 209 Polonium	84 At 210 Astatine	85 Rn 222 Radon									
87 Fr 223 Francium	88 Ra 226 Radium	89 Ac 227 Actinium	103 Rf 261 Rutherfordium	104 Db 268 Dubnium	105 Sg 271 Seaborgium	106 Bh 274 Bohrium	107 Hs 277 Hassium	108 Mt 288 Meitnerium	109 Ds 291 Darmstadtium	110 Cn 285 Copernicium	111 Nh 286 Nihonium	112 Fl 289 Flerovium	113 Uut 288 Ununtrium	114 Uuq 289 Ununquadium	115 Uup 289 Ununpentium	116 Uuh 291 Ununhexium	117 Uus 294 Ununseptium	118 Uuo 294 Ununoctium								
Lanthanide Series		57 La 138.905 Lanthanum	58 Ce 140.12 Cerium	59 Pr 140.908 Praseodymium	60 Nd 144.242 Neodymium	61 Pm 145 Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.925 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.930 Holmium	68 Er 167.259 Erbium	69 Tm 168.933 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.967 Lutetium										
Actinide Series		89 Ac 227 Actinium	90 Th 232.037 Thorium	91 Pa 231.036 Protactinium	93 U 238.029 Uranium	94 Np 237 Neptunium	95 Pu 244 Plutonium	96 Am 243 Americium	97 Cm 247 Curium	98 Bk 247 Berkelium	99 Cf 251 Californium	100 Es 252 Einsteinium	101 Fm 257 Fermium	102 Md 258 Mendelevium	103 No 259 Nobelium	104 Lr 262 Lawrencium										



Refer to the note

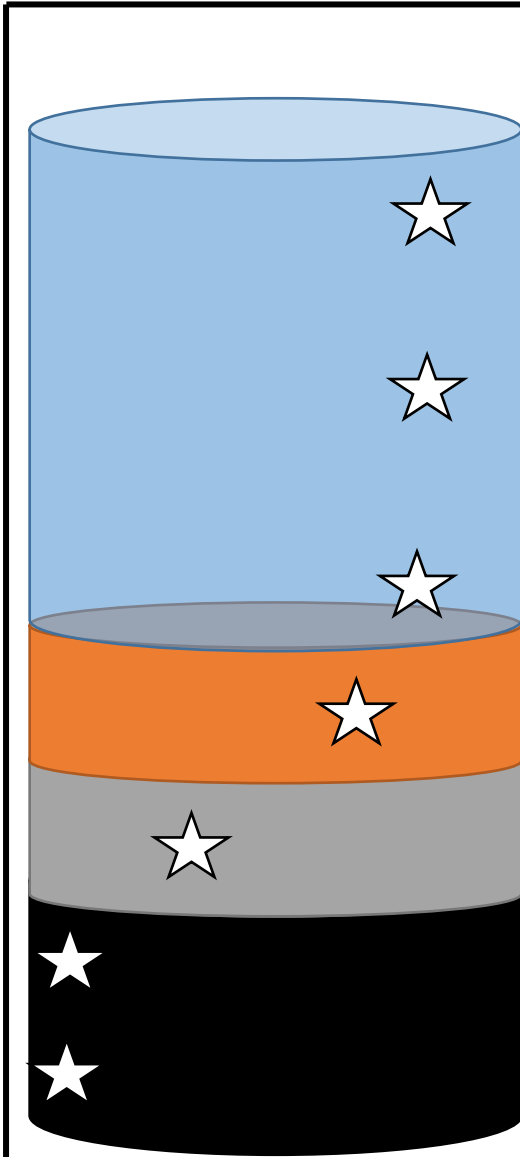
pH of Natural Waters

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



Dissolved O₂ (mg/L)

Depth (cm)



Sediments under a water column

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

- Driven by O₂ gas availability
- **Oxic** – O₂ gas present
- “oxidizing” environment
- **Suboxic** – low O₂ gas present; respiration with O₂ is hindered
- **Anoxic** – no O₂ present; organisms “breathe” other chemicals
- “reducing” environment

Refer to the note

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^+		

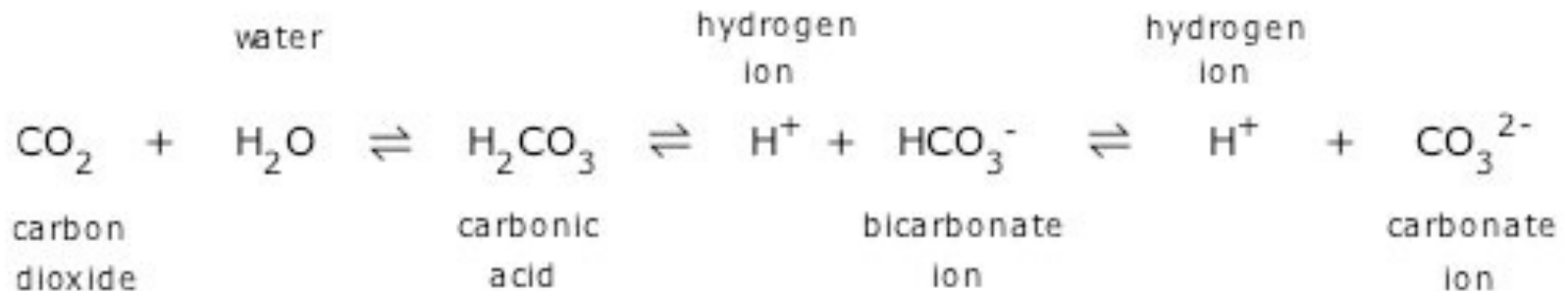
Minor solutes of utmost importance: Al, Fe, Mn

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



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

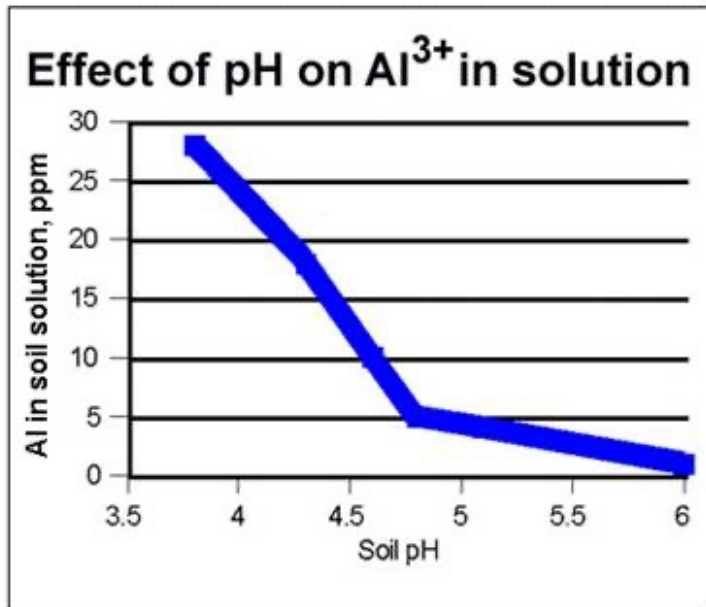
- Cl^-
- Non-reactive in the environment, hence a “conservative” ion
- Mostly input to surface waters from precipitation

Dissolved silica (aka silicic acid)

- $\text{Si}(\text{OH})_4^0$
- 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, $\text{Al}(\text{OH})_3$, 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



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

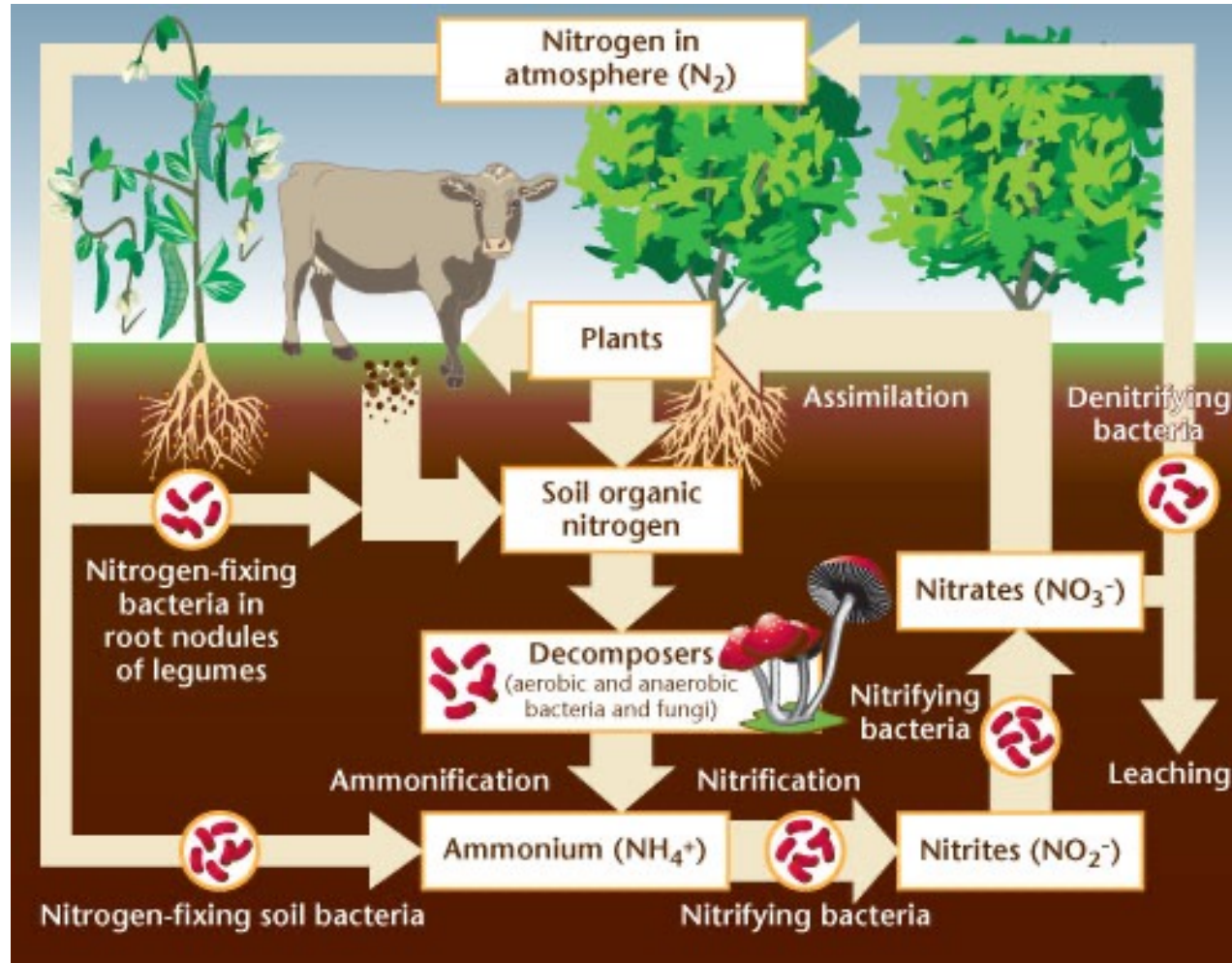


Manganese - exists in water primarily as Mn^{2+}

- 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

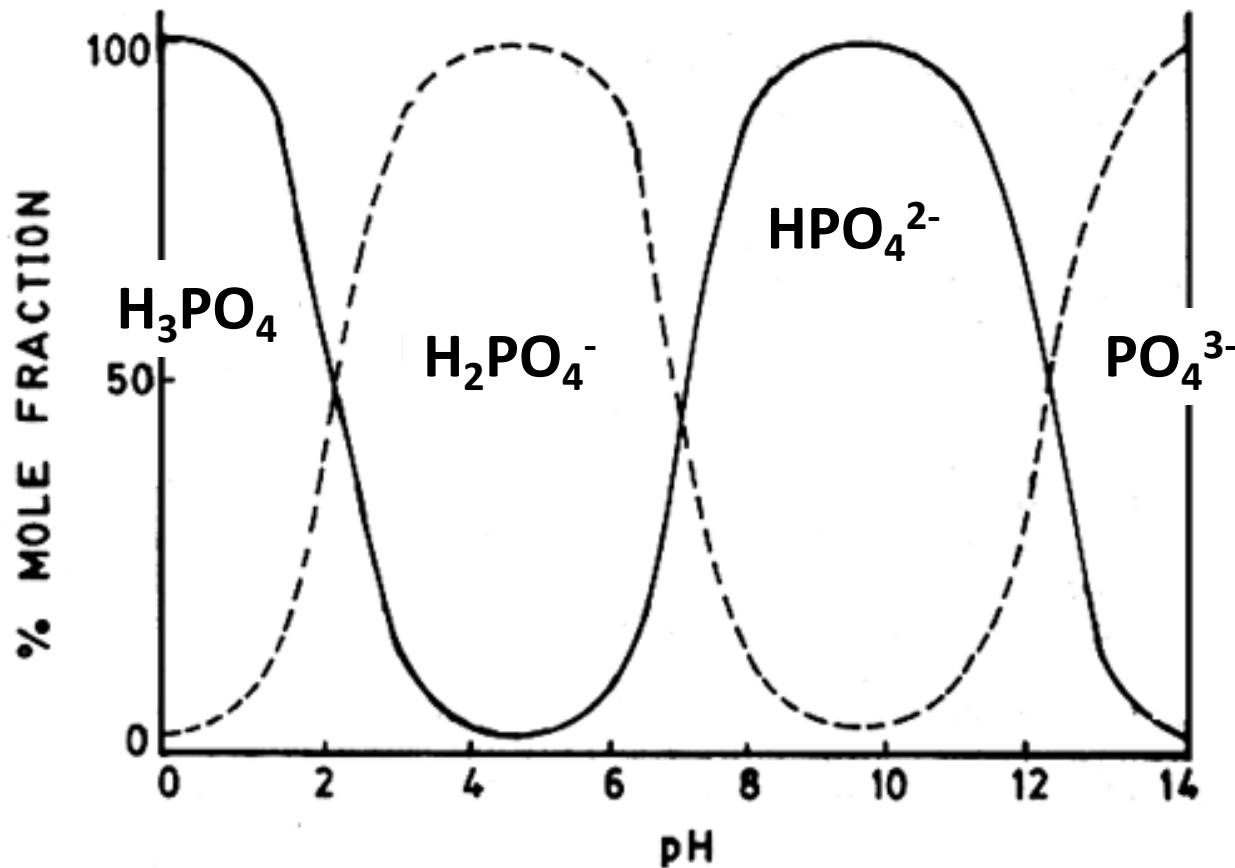
Nitrogen

- 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/>