GEOL 414/514

GENERAL CONTROLS ON NATURAL WATER CHEMISTRY

Chapter 8

LANGMUIR

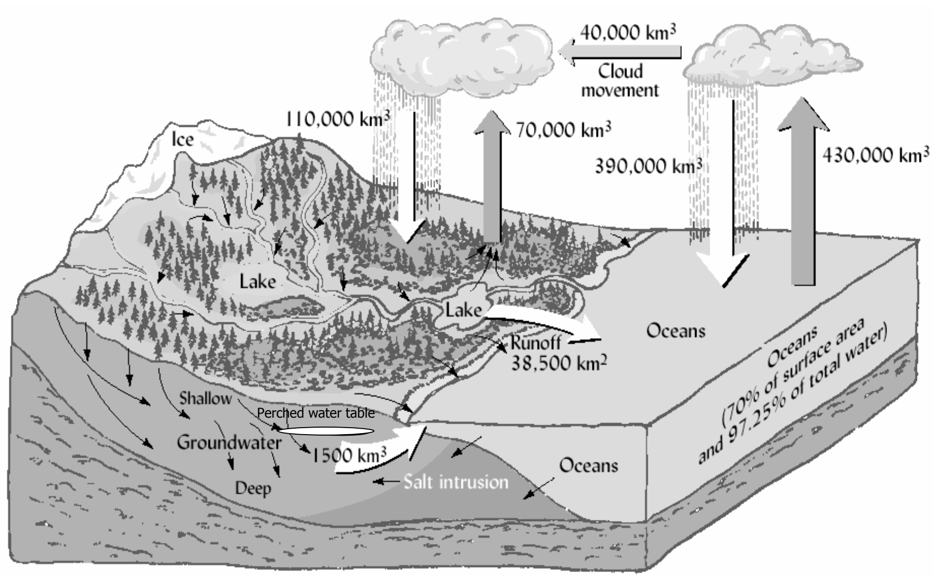
HYDROLOGIC CYCLE, RESIDENT TIME & WATER-ROCK RATIO

- **The hydrologic cycle involves the movement of water between reservoirs**
- **The residence time (t_R) in each reservoir is defined as:**

$$t_R = \frac{\text{amount of water in reservoir (g)}}{\text{flux into reservoir (g/time)}}$$

Reservoir	t_R (years)
ocean	3550
atmosphere	11 days
groundwater	1700

THE HYDROLOGIC CYCLE



WATER IN THE HYDROSPHERE

- **Review terms in Section 8.2**
- **The time that it takes for nature to clean up stable chemical pollutants will be directly proportional to reservoir residence time**
- **Water budget for groundwater recharge:**

I	=	P	±	R	-	ET	-	MR
Ground-water Recharge		precipi-tation		runoff		evapo-trans-piration		moisture retention

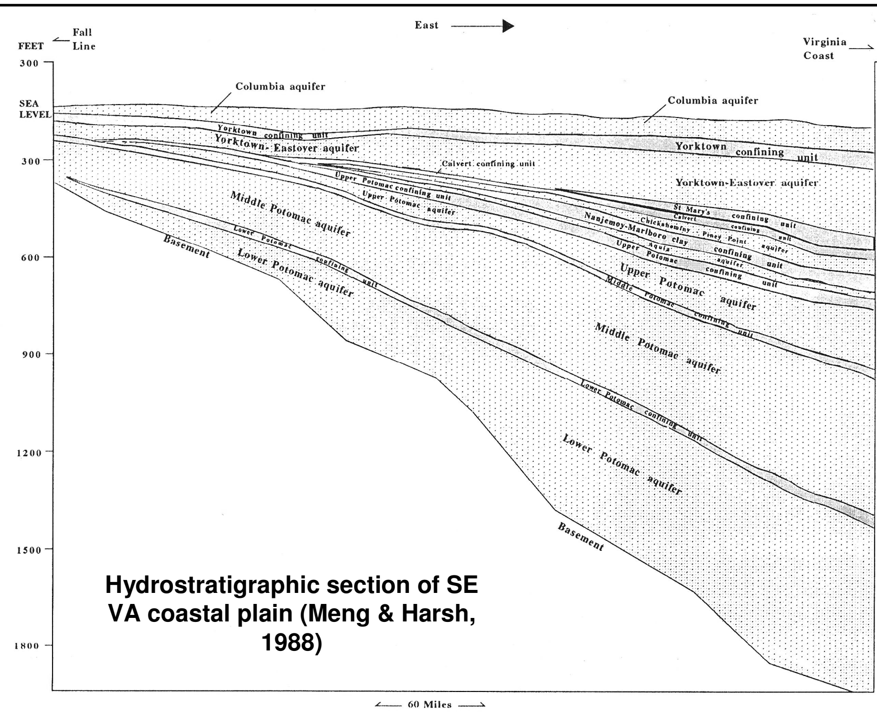
- **Author notes that runoff can either add to or subtract from infiltration; difficult to understand how runoff can cause infiltration - must define area for recharge**

CONTROLS ON THE COMPOSITION OF SUBSURFACE WATERS

Composition of subsurface waters is a function of:

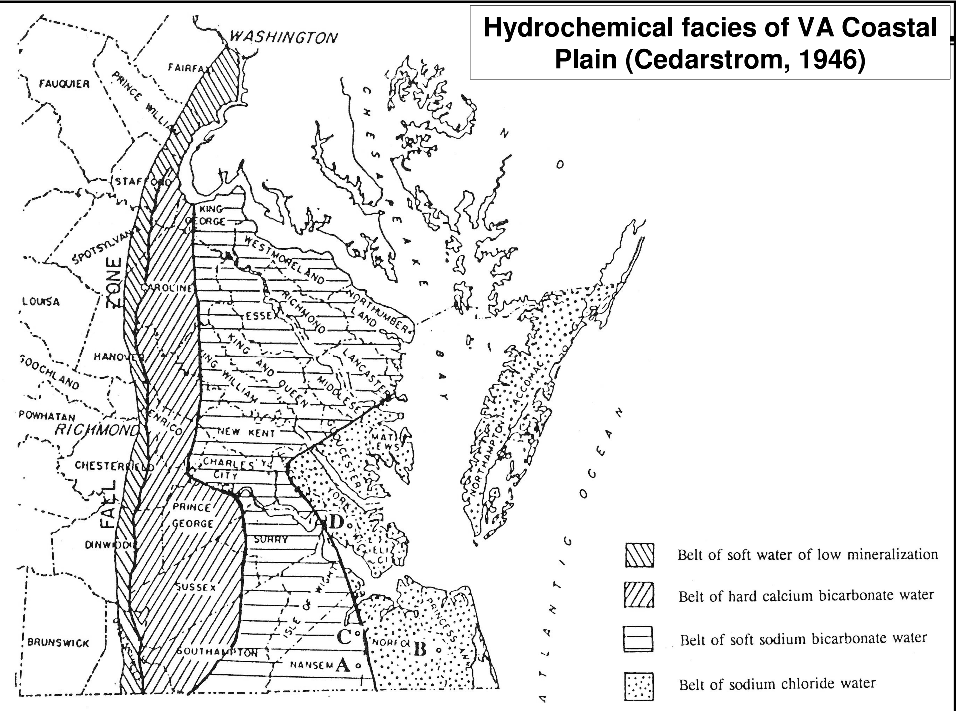
1. **Composition of groundwater recharge**
2. **Petrologic & mineralogic composition of subsurface rocks - small amounts of soluble minerals have significant influence**
3. **Hydrologic properties of rocks - flow velocities - see Table 8.1**

Note examples in text; we'll examine the F concentrations in the Middle Potomac Aquifer in SE VA



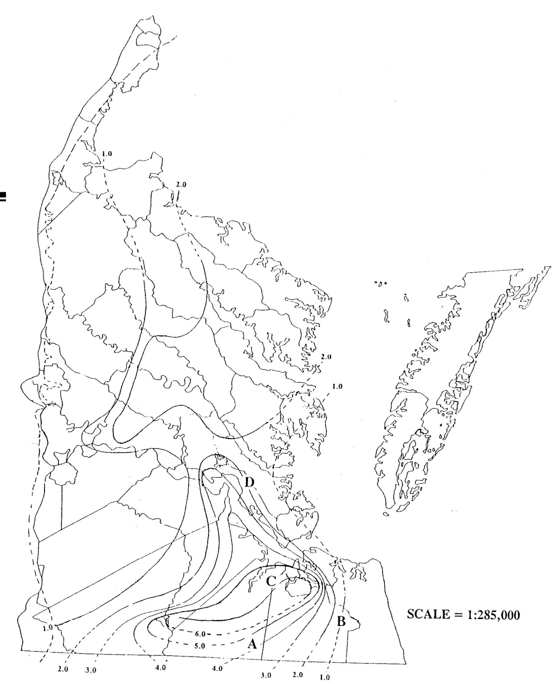
Hydrostratigraphic section of SE VA coastal plain (Meng & Harsh, 1988)

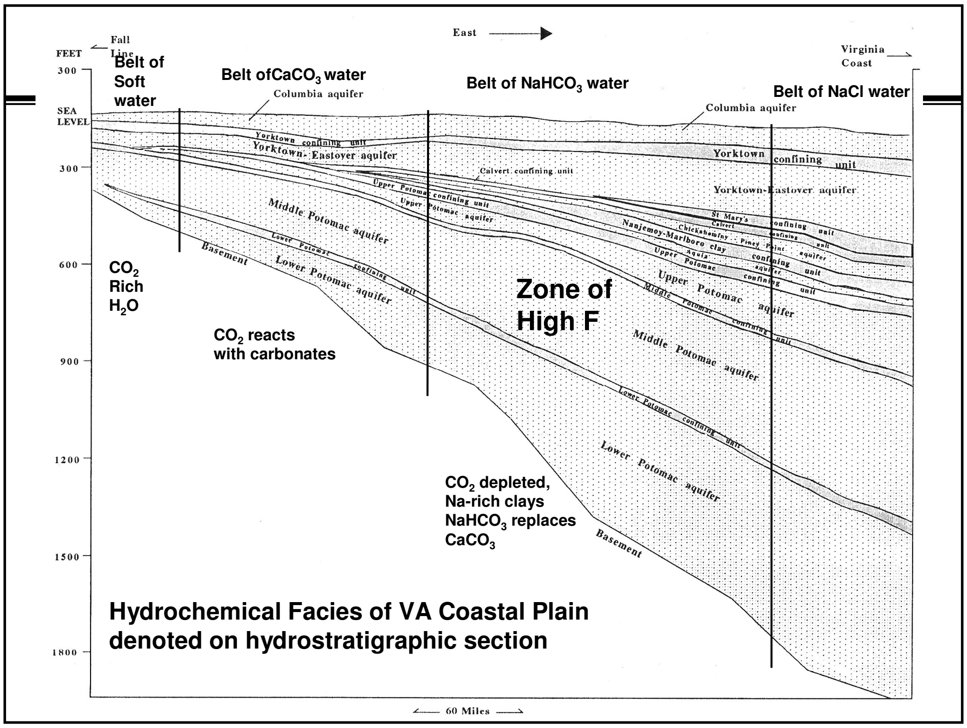
Hydrochemical facies of VA Coastal Plain (Cedarstrom, 1946)



Groundwater F distribution in the Middle Potomac Aquifer, VA

Concentrations in mg/L





PRECIPITATION CHEMISTRY & ACID RAIN

- **What is pH of rainwater, assuming that acidity is only from CO_2 at P_{atm}?**

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

- **Assume that the second K_d is not important**

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

$$4.7 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{2.04 \times 10^{-5}} \qquad [H^+] = [HCO_3^-]$$

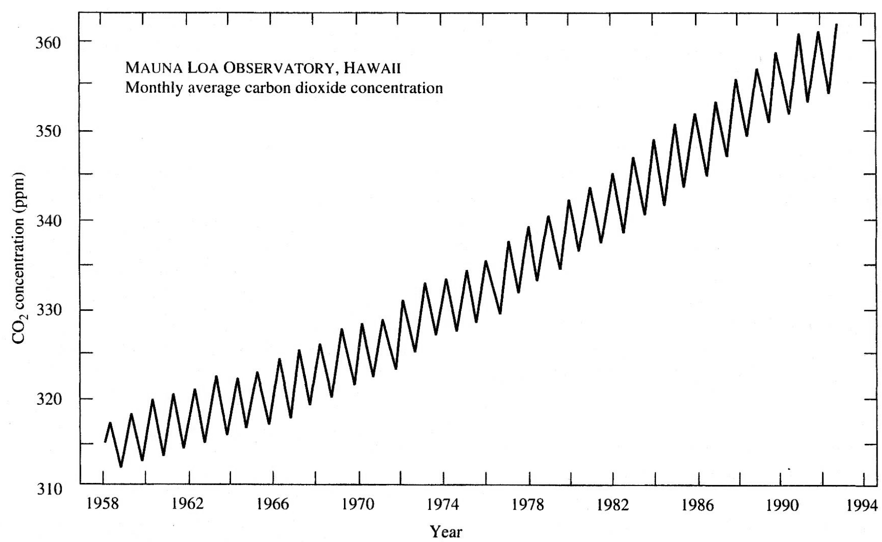
$(4.7 \times 10^{-7}) * (2.04 \times 10^{-5}) = [H^+]^2$

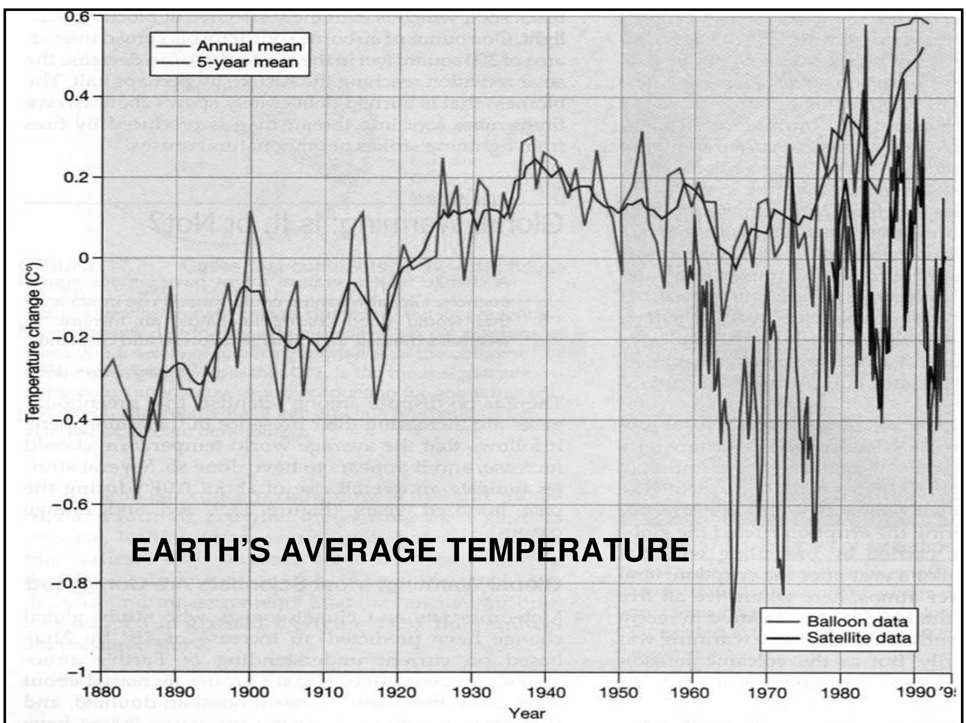
$[H^+]^2 = 8.57 \times 10\text{-}12$

$[H^+] = 2.92 \times 10\text{-}6$

pH = 5.53

GENERAL COMPOSITION OF PRECIPITATION - ATMOS CO_2





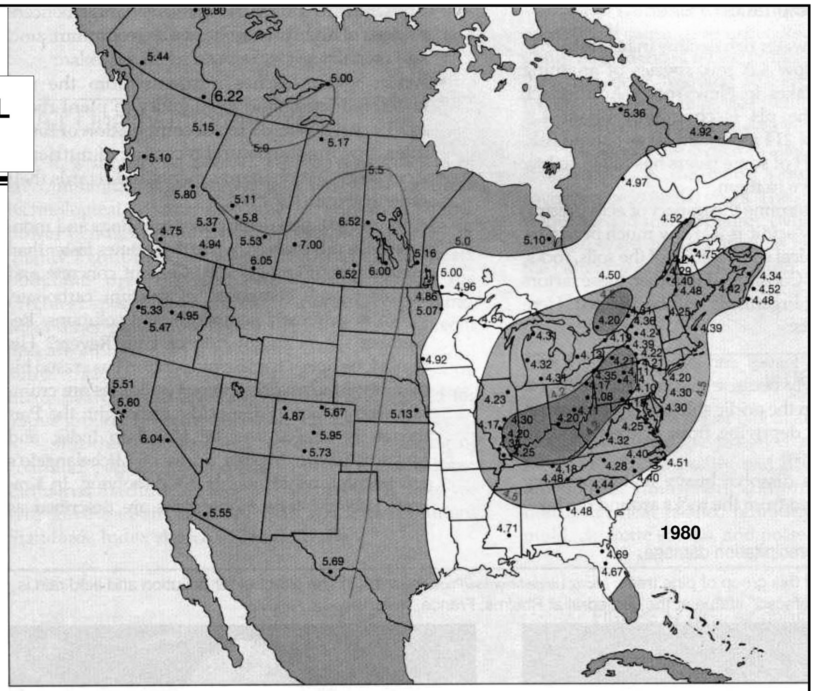
GENERAL COMPOSITION OF PRECIPITATION

- Major constituents of rainfall are Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, NH_4^{+}, H^{+}, Cl^{-}, NO_3^{-}, SO_4^{-2}, sometimes HCO_3^{-}
- See Figs 8.6 & 8.7 for isoconcentration contours for Na^{+}, Cl^{-}, SO_4^{-2} & NO_3^{-} in contiguous USA ppt'n
- Globally, one-half of SO_4^{-2} is derived from combustion of fossil fuels & 1/2 from natural sources
- Anthropogenic sources responsible for 90% atmos SO_4^{-2} deposition in eastern N. America
- USA emissions of SO_2 & NO_x are decreasing, slowly; may also be declining in Europe
- Global emissions of SO_2 are significantly increasing

ACID PRECIPITATION

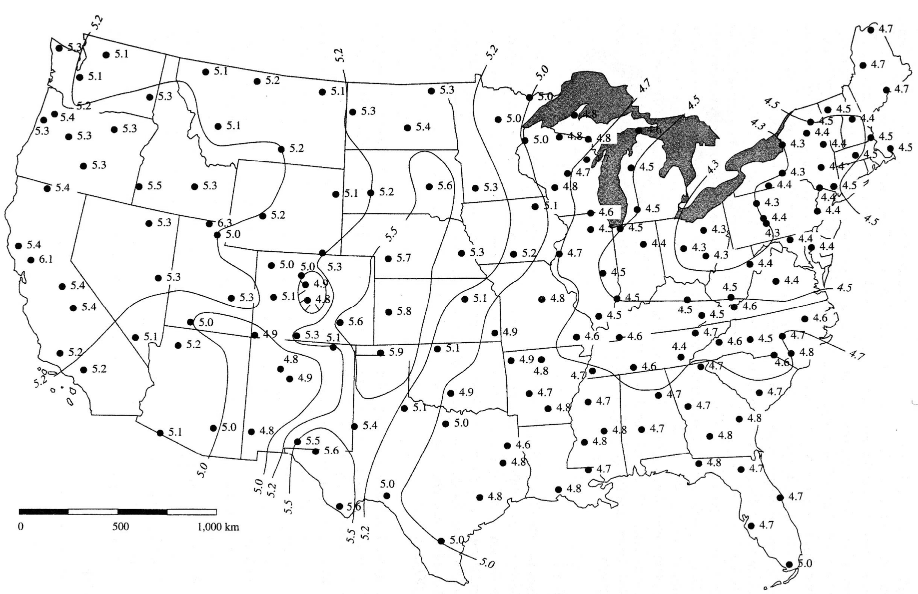
- Acid rain, snow, fog; rain most prevalent
- Rain more acid than pH 5.7 from reactions of gases SO_2, NO_2, NO (NO_x) & to a lesser extent, HCl
- Forms in rain: H^{+}, SO_4^{-2}, NO_3^{-}, Cl^{-}
- Initial rainfall is most acid, short rainfall events deposit higher H^{+} concentrations
- Hopewell, VA, 1985, rainfall pH = 3.2, short rainfall event
- Causes serious damage to stone buildings, monuments, metal structures, soils, surface waters
- Rainfall pH has been slowly increasing over the past several years but still is <4.5 over much of the eastern US

RAINFALL pH IN US



This map of pH reveals a pattern of air pollution.

Avg pH of rainfall in contiguous USA for 1995



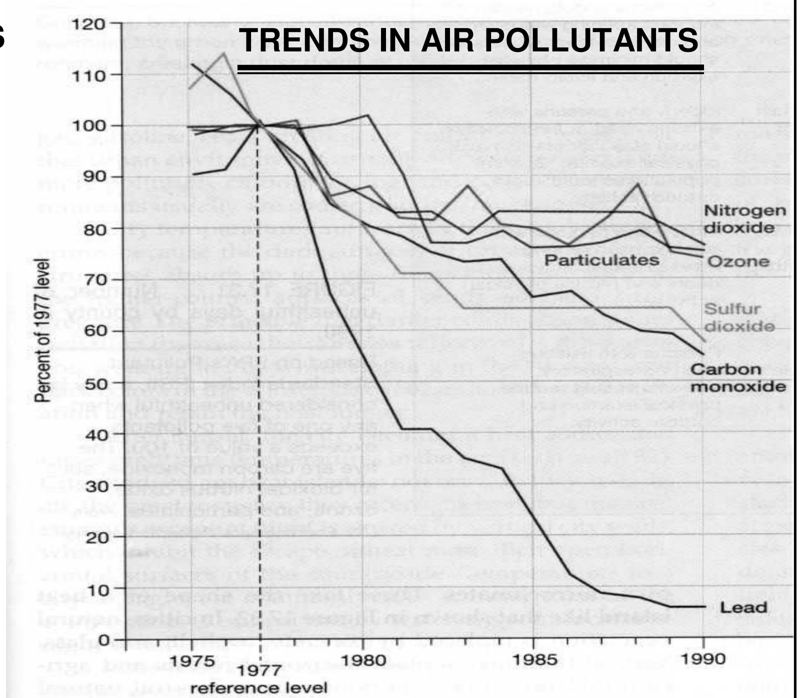
TRACE ELEMENTS IN RAIN

- Most trace elements are deposited from atmos in particulate form; some are true gases
- An atmospheric enrichment factor is computed in Fig 8.11
- Elements having the greatest tendency for mobility in gaseous forms are Cd, Se, As & Hg; moderate tendency for Sb, Zn, Pb, Ni & V
- The burning of fossil fuels, smelting of metal ores & incineration of urban wastes are primary anthropogenic sources
- Atmos Pb increased 200X from industrialization & have recently decreased 7.5X in USA
- Rate of atmos Hg deposition inc'd 3.4X since 1850

SUCCESS STORY!

LEAD LEVELS IN THE ATMOS. SHOW GREAT DECLINE

TRENDS IN AIR POLLUTANTS



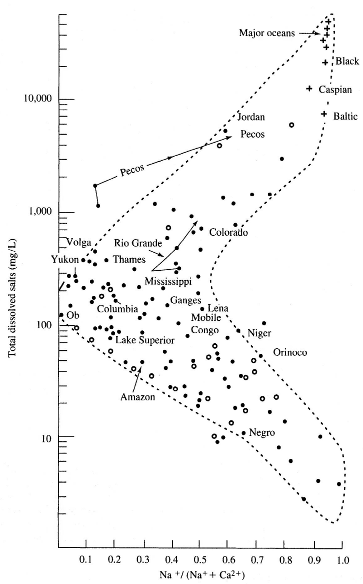
GENERAL CHEMISTRY OF SURFACE- & GROUNDWATERS

TABLE 8.8 Median values of pH and TDS and of major (>1 mg/L) constituents in surface waters and groundwaters

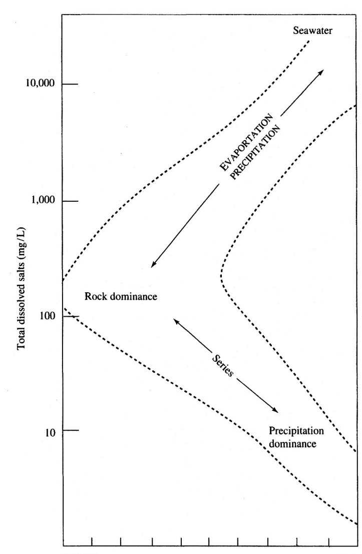
Major Constituents		
Constituent or parameter	Surface-water (mg/L)	Groundwater (mg/L)
HCO_3^-	58	200
Ca^{2+}	15	50
Cl^-	7.8	20
K^+	2.3	3
Mg^{2+}	4.1	7
Na^+	6.3	30
SO_4^{2-}	3.7	30
$SiO_2(aq)$	14	16
pH	—	7.4
TDS	120	350

Notable trace elements (μg/L): Fe, F, Sr - See Table 8.8 in text

CONTROLS ON CHEMICAL COMPOSITION OF RIVERS



Gibbs explaination of general controls of streams & rivers



WATER QUALITY VS QUANTITY

- Water quality & quantity are inherently interdependent
- Often we may need to reconstruct the amounts of two or more waters that have mixed to create another
- Mixing is described by mass-balance equation:

$$C_m V_m = C_1 V_1 + C_2 V_2$$

- Since $V_m = V_1 + V_2$, V_m may be eliminated to give:

$$R_V = \frac{V_1}{V_2} = \frac{(C_2 - C_m)}{(C_m - C_1)}$$

- R_V & vol ratios can be determined from the chem anal of a single conservative (Cl^-, Br^-) species in all three waters

WATER QUALITY VS QUANTITY

- Changes in flow rate or discharge of stream or GW are usually accompanied by changes in water quality
- Influence on streams may switch between GW and runoff depending on rainfall
- There are usually dilution effects for dissolved constituents and increased conc's for elements assoc'd with sediments with increased flow
- For overland flow & interflow causing dilution:

$$\log C_m = \log C_1 Q_1 - \log Q_m$$

- With constant baseflow discharge & composition, this is eq'n of straight line w/ slope = -1 & intercept = $\log C_1 Q_1$ (see Figs 8.16 & 8.17)

IMPORTANCE OF DEFINING BACKGROUND WATER QUALITY

- Many surface & GWs contain natural conc's that exceed the EPAs drinking water standards
- Major question often is how to determine natural (BG) levels
  - how do we assure ourselves that a given location is truly unaffected by human influences?
  - how do we determine that elevated conc's are due to natural causes?
  - often difficult in populated areas
  - for large sample sets can use cumulative frequency plots or frequency distribution plots to ID different "populations"