Updated: 22 January 2020

Print version

CEE 680: Water Chemistry

Lecture #2

Intro: Expressions of Concentrations and Natural Abundance

(Stumm & Morgan, Chapt.1 & 3.4)

(Pg. 4-11; 97-105)

(Pankow, Chapt. 2.8)

(Benjamin, 1.2-1.5)

Elemental abundance in fresh water

From: Stumm & Morgan, 1996; Benjamin, fig 1.4; Langmuir figure 8.12

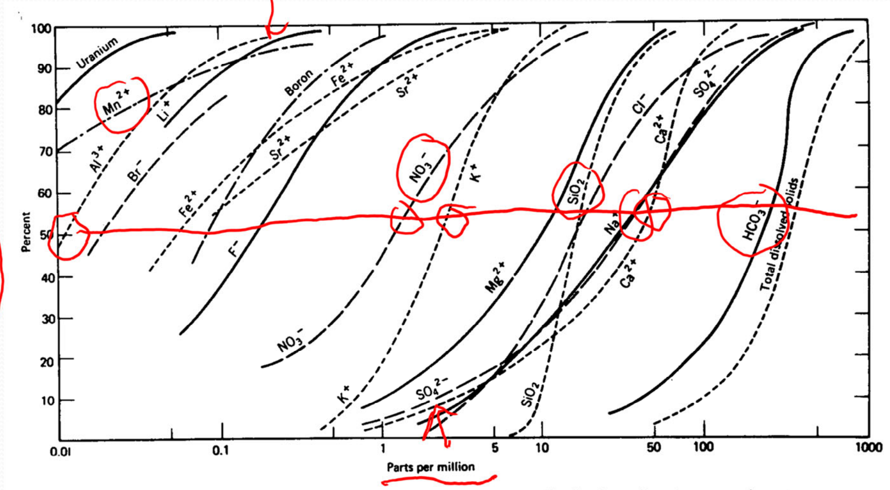
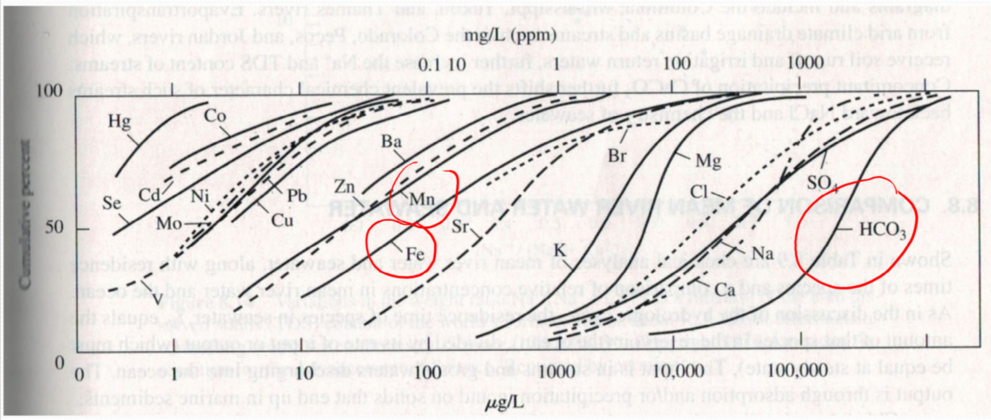


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Same, but for groundwater

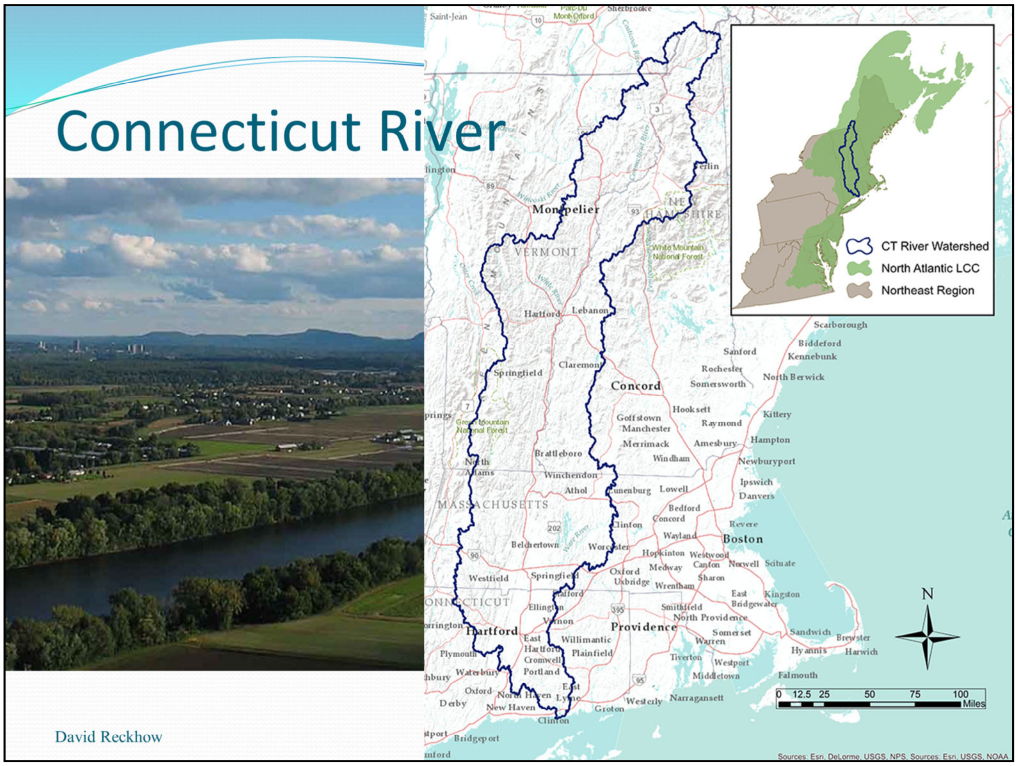
- From Langmuir, figure 8.13
  - Based on Rose et al., 1979, Geochemistry in mineral exploration



Connecticut River vs Vaal River

- Connecticut River (CT River) watershed
  - Ryder et al., 1981
- Vaal River, site C1H001
  - Mohr, 2015
- Avg (surface water) SW
  - Turekian, 1977 & Langmuir, pg 294
- Precipitation & Sea Water
  - Benjamin, Table 1.1
- All values in mg/L

Parameter	CT River	Vaal River	Avg SW	Precip	Sea Water
Sodium	6.5	4.7	6.3	9.4	10,800
Potassium	1.3	0.9	2.3		395
Calcium	13	7.1	15	0.8	408
Magnesium	3.2	5.5	4.1	1.2	1280
Chloride	10	4.5	7.8	17	19,400
Bicarbonate	22	50	58	2.0	72
Sulfate	27	7.4	3.7	7.6	2710
TDS	113	79	120	38	35,000
Na/(Na+Ca)	0.33	0.40	0.30	0.92	0.96


Connecticut River
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CT River Watershed
North Atlantic LCC
Northeast Region
N
0 12.5 25 50 75 100
Miles

- sda

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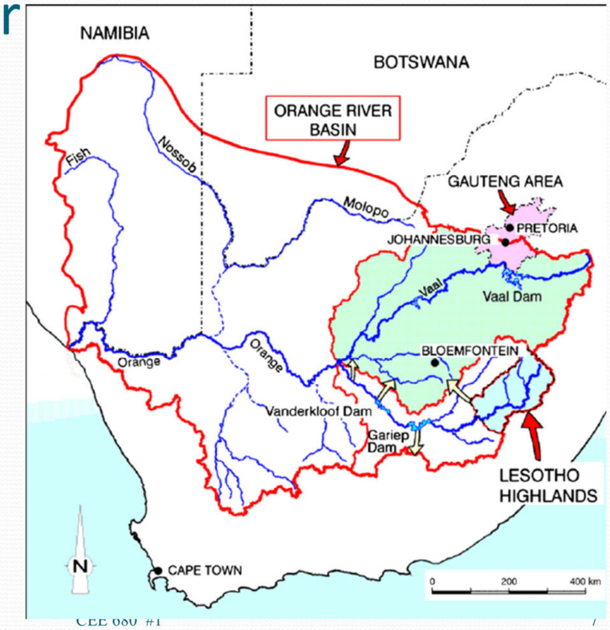
Orange River

- Vaal River sub basin



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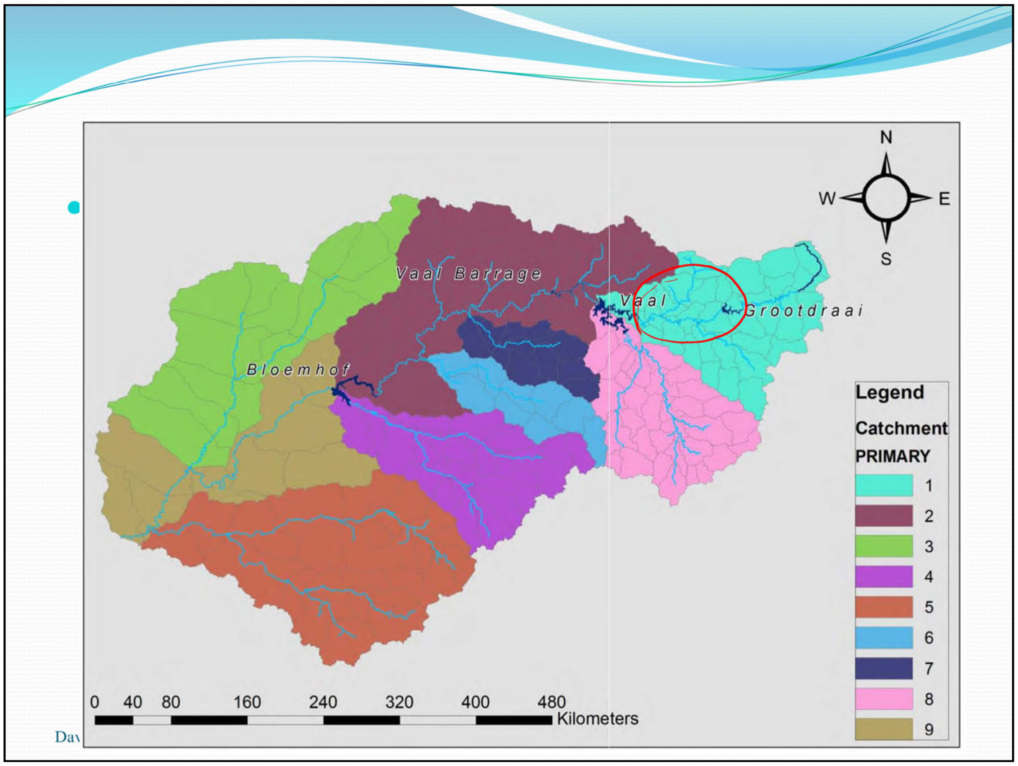
N
W
E
S
Vaal Barrage
Vaal
Grootdraai
Bloemhof
Legend
Catchment
PRIMARY
1
2
3
4
5
6
7
8
9
0 40 80 160 240 320 400 480
Kilometers

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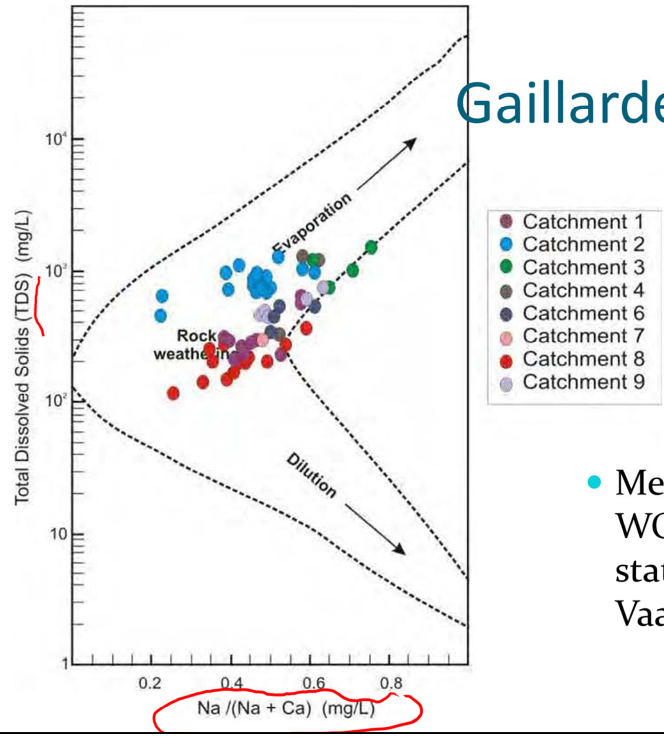
Gaillardet Diagram



- Median values for WQ monitoring stations along the Vaal River

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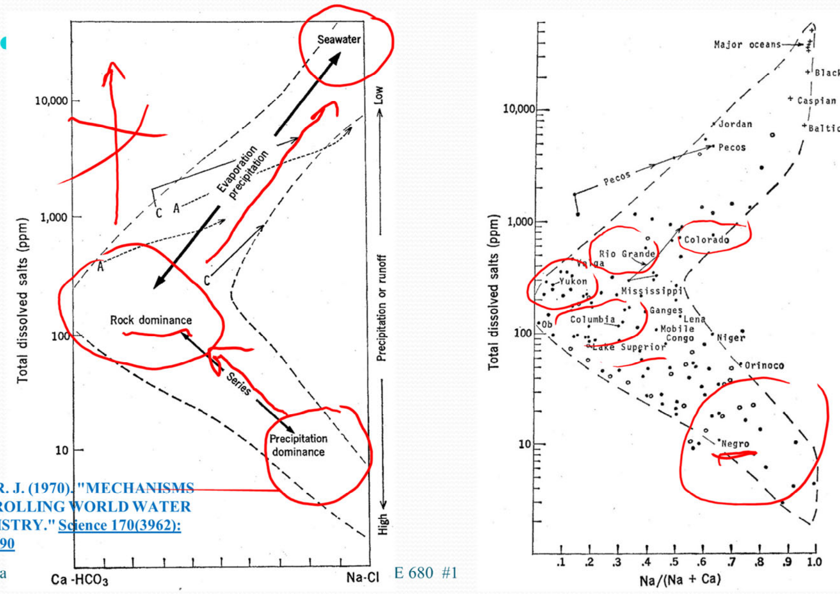
Gibbs view of water composition



Gibbs, R. J. (1970). "MECHANISMS CONTROLLING WORLD WATER CHEMISTRY." Science 170(3962): 1088-1090

Stoichiometry: Lake Example

- Basic limnology tells us that phosphorus stimulates algal growth, they produce O_2, and bacteria consume O_2 when the algae die
- If we add 1 mg P to a small lake
  - How much algal biomass is produced?
  - How much O_2 is produced?
  - How much O_2 is later consumed?
- Elemental analysis of algae: empirical formula
  - $C_{106}H_{263}O_{110}N_{16}P$

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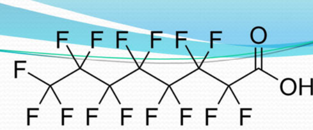
Solution

- Balance equation
  - $106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+ =$ $C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$
- Use stoichiometric coefficients
  - Biomass: $= 1mg-P\left(\frac{1mmole-P}{31mg-P}\right)\left(\frac{3551mg-algae}{1mmole-algae}\right)\left(\frac{1mmole-algae}{1mmole-P}\right)$
    $= 115mg-algae$
  - O_2 production: $= 1mg-P\left(\frac{1mmole-P}{31mg-P}\right)\left(\frac{32mg-O_2}{1mmole-O_2}\right)\left(\frac{138mmole-O_2}{1mmole-P}\right)$
    $= 142mg-O_2$
  - O_2 consumption:

Talk about oxygen consumption in return to starting materials

PFOA



In NY village, trail of cancer leads to tap water

By MARY ESCH
Associated Press

HOOSICK FALLS, N.Y. – After his factory worker father died a painful death from kidney cancer at age 68 in 2013, Michael Hickey made it his mission to find out why so many people in his hometown along the Hoosic River were getting sick.

Two years later, the U.S. Environmental Protection Agency has warned residents of Hoosick Falls not to drink or cook with water from municipal wells, and a plastics plant has agreed to install a $2 million carbon filtration system at the village water treatment plant.

Hickey's campaign began with suspicion about industrial pollution in the factory village near the Vermont border. His father had worked for 35 years at a plant that made high-performance plastics similar to Teflon, so Hickey searched online for "cancer" and "Teflon."

What he found: PFOA.

Perfluorooctanoic acid, a water and oil repellent, had been used since the 1940s in products including non-stick cookware, stain-resistant carpeting and microwave popcorn bags. Manufacturers agreed to phase it out by the end of 2015 shortly after DuPont reached a $16.5 million settlement with the EPA over the company's failure to report possible health risks associated with PFOA.

A scientific panel that conducted health studies as part of a DuPont settlement of a West Virginia class-action lawsuit concluded there was a "probable link" between PFOA exposure and kidney cancer, testicular cancer, thyroid disease, high cholesterol, ulcerative colitis and pregnancy-induced hypertension.

In Hoosick Falls, nobody has ever scientifically documented that the village has an unusually high cancer rate, but Hickey and a local doctor had heard enough anecdotal evidence that they felt it should be addressed.


AP PHOTO
A mural of a Grandma Moses painting adorns a building in Hoosick Falls, N.Y.

"There's always been talk around town about how there's a lot of cancer," Hickey said. "When my dad, who didn't drink or smoke, was diagnosed with kidney cancer, that made it more personal."

Dr. Marcus Martinez, the family doctor for many of the village's 3,500 residents, added there certainly seemed to be a high rate of cancer there, particularly rare, aggressive forms. The 44-year-old Martinez himself is in remission from aggressive prostate cancer.

When the two men suggested testing the village water supply, part-time Mayor David Borge at first refused, citing state guidelines. New York state classifies PFOA as an "unspecified organic contaminant" and doesn't require testing for it.

The EPA has a non-enforceable guidance level of 400 parts per trillion — roughly 4 teaspoons in enough water to fill a 10-mile string of rail tankers.

Hickey used his own money in summer 2014 to have water from his kitchen tap and other sources tested. The results showed PFOA at 540 ppt from Hickey's home, exceeding the EPA's guidance. Village officials subsequently tested the municipal supply and found PFOA at similar levels.

Saint-Gobain Performance Plastics, part of a Paris-based global conglomerate, in 1999 became the fifth owner of a plastics factory in Hoosick Falls. It conducted tests in the summer of 2015 and reported a PFOA level of 18,000 ppt in groundwater under its plant, 500 yards from the village's main water wells.

"Saint-Gobain Performance Plastics is committed to helping the village of Hoosick Falls with this situation," company spokesman Carmen Ferrigno said. While the source of the PFOA contamination hasn't been identified, Saint-Gobain has been paying for bottled water for residents since November and has agreed to pay for filtration to remove the chemical from the public water supply, he said.

Hickey and Martinez, along with Albany environmental lawyer David Engel, weren't satisfied. They wanted people to be told not to drink the tap water, as well as a full investigation and remediation.

Engel contacted Judith Enck, who heads the EPA region that includes New York. She issued a statement in December warning residents not to drink or cook with village water. Until then, state and village officials had told residents the water was unlikely to cause health problems.

On Jan. 14, Enck and a panel of leading EPA scientists addressed a standing-room-only crowd at Hoosick Falls' high school auditorium. The same day, New York officials asked the EPA to add the Saint-Gobain plant and other possible sources of contamination in Hoosick Falls to the Superfund priorities list. The state health department also recently announced plans to study cancer rates in the village and vicinity.

"We are giving this contamination problem a high priority," Enck said. "A very detailed study of groundwater is needed in Hoosick Falls to know what we are dealing with and how to best address it."

Perfluorooctanoic acid (**PFOA**), also known as **C8** and **perfluorooctanoate**, is a synthetic compound. One industrial application is as a surfactant in the production of fluoropolymers. It has been used in the manufacture of such prominent consumer goods as polytetrafluoroethylene (commercially known as Teflon). PFOA has been manufactured since the 1940s in industrial quantities.

PFOA persists indefinitely in the environment. It is an animan carcinogen. PFOA has been detected in the blood of more than 98% of the general US population in the low and sub-ppb range, and levels are higher in chemical plant employees and surrounding subpopulations. How general populations are exposed to PFOA is not completely understood. PFOA has been detected in industrial waste, stain resistant carpets, carpet cleaning liquids, home dust, microwave popcorn bags, water, food, some cookware and PTFE such as Teflon.

Daily Hampshire Gazette, 27 January 2016

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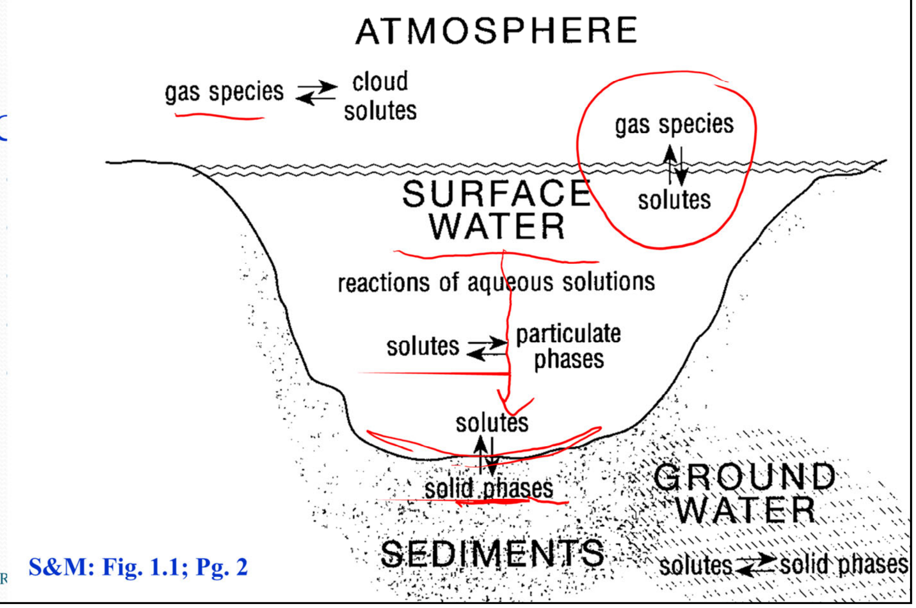
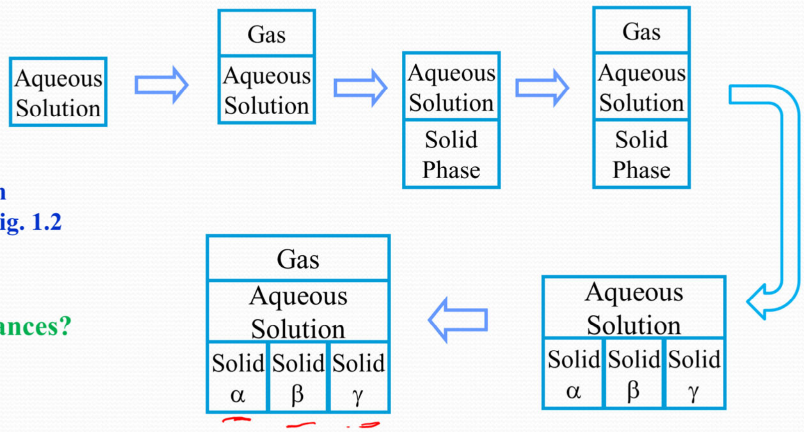
Natural Water Environment



S&M: Fig. 1.1; Pg. 2

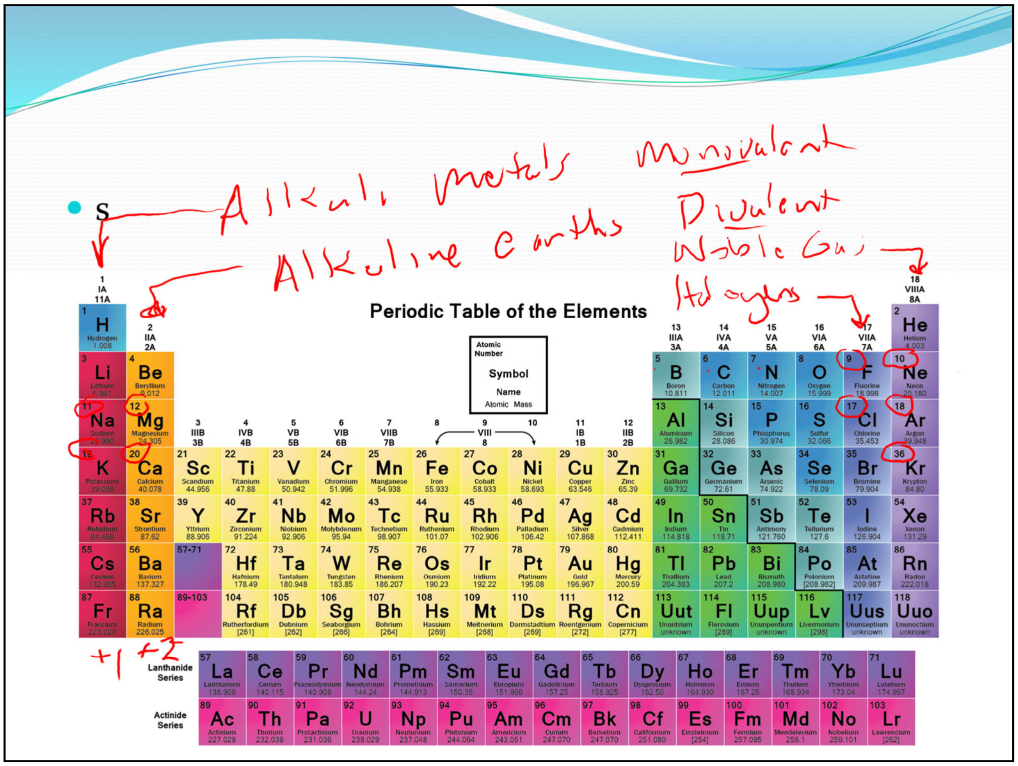
Model Complexity: Phases

- Single Phase to multi-phase

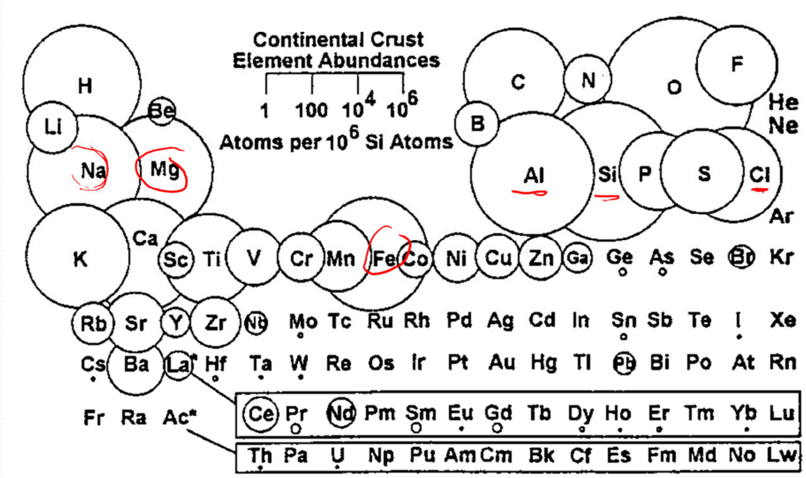


Based on S&M: Fig. 1.2 Pg. 4

Abundances?


S
Alkali metals
Monovalent
Alkaline earths
Divalent
Noble Gas
Halogens
Periodic Table of the Elements
+1 +2
Lanthanide Series
Actinide Series

Elemental abundance in crust



- O
- Si
- Al
- Fe
- Ca
- Na
- Mg
- K
- Ti
- H
- P
- Mn
- F

Elemental abundance in fresh water

From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1

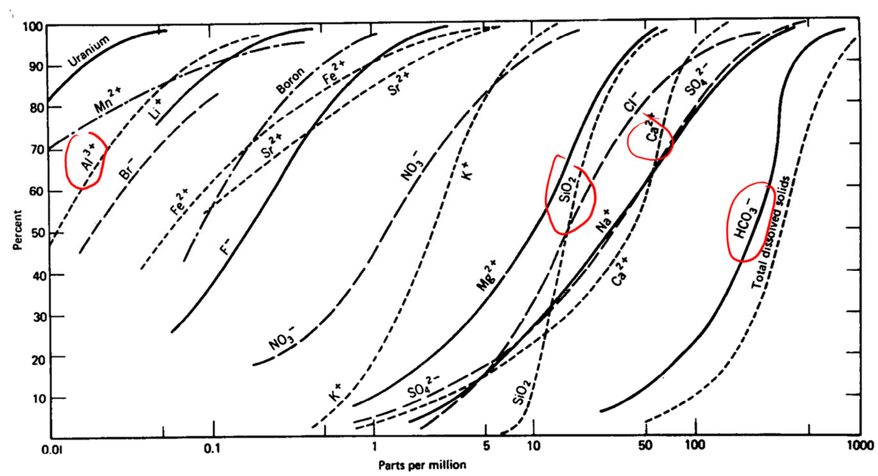


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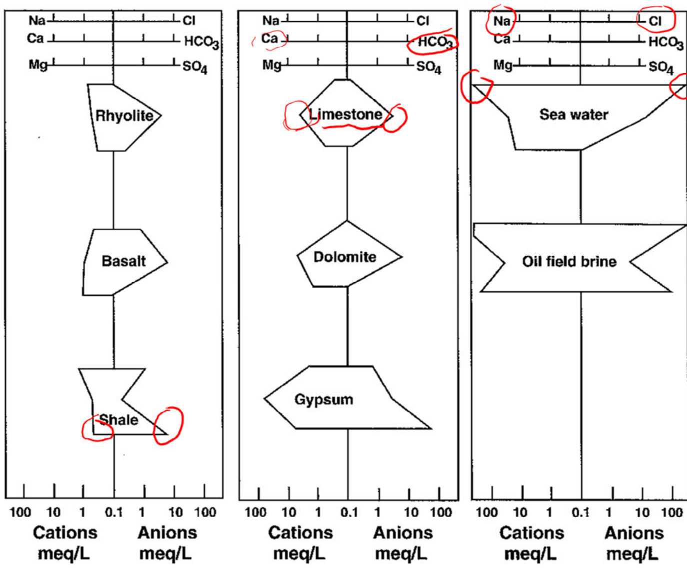
Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Rock-WQ Connection



- Water Solutes reflect rock mineralogy; e.g.
  - Limestone
    - $CaCO_3$, mostly
  - Dolomite
    - $CaMg(CO_3)_2$, mostly
  - Gypsum
    - $CaSO_4$

"Stiff diagram"
From Hounslow, 1995
Water Quality Data; Analysis and Interpretation

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Review

- Units
  - Mass based
  - Molarity
  - Molality
  - Normality
  - Mole fraction
  - Atmospheres
- Chemical Stoichiometry
  - mass balance
  - balancing equations
- Thermodynamics
  - law of mass action
  - types of equilibria

SI Unit prefixes

Factor	Prefix	Symbol
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

Factor	Prefix	Symbol
10^{1}	deka	da
10^{2}	hecto	d
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E

Mass Based Concentration Units

- Solid samples

$$\frac{17.5mg\ \text{Pb}}{1kg\ \text{soil}} = \frac{17.5x10^{-3}\ \text{g Pb}}{1\text{x}10^{3}\ \text{g soil}} = 17.5g\ \text{Pb} \Big/ 10^{6}\ g\ \text{soil}$$

$$= 17.5\ \text{ppm}_{\text{m}}\ \text{Pb in soil}$$

$$1mg/kg = 1ppm_m$$
$$1\mu g/kg = 1ppb_m$$

- Liquid samples

Density of Water at 5ºC

$$\frac{0.35mg\ \text{Fe}}{1L\ \text{water}} x \frac{1L\ \text{water}}{10^3\ \text{g water}}$$

$$= \frac{0.35mg\ \text{Fe}}{10^3\ \text{g water}} = \frac{0.35x10^{-3}\ \text{g Fe}}{10^3\ \text{g water}} = 0.35g\ \text{Fe} \Big/ 10^6\ g\ \text{water}$$

$$= 0.35\ \text{ppm}_m\ \text{Fe in water}$$

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Mass/Volume Units	Mass/Mass Units	Typical Applications
g/L (grams/liter)	(parts per thousand)	Stock solutions
mg/L (milligrams/liter) 10^{-3}g/L	**ppm** (parts per million)	Conventional pollutants (DO, nitrate, chloride)
µg/L (micrograms/liter) 10^{-6}g/L	**ppb** (parts per billion)	Trihalomethanes, Phenols.
ng/L (nanograms/liter) 10^{-9}g/L	**ppt** (parts per trillion)	PCBs, Dioxins
pg/L (picograms/liter) 10^{-12}g/L		Pheromones

Gas phase concentration

- Gas samples (compressible)

$$\frac{0.056\ mg\ \text{Ozone}}{1 m^3\ \text{air}}$$

  - Could be converted to a ppm_m basis
    - But this would change as we compress the air sample
  - Could also be converted to a ppm_v basis
    - Independent of degree of compression
    - But now we need to convert mass of ozone to volume of ozone

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By definition:

$$n = \frac{mass(g)}{GFW}$$

Ideal Gas Law

- An ideal gas
  - Will occupy a certain fixed volume as determined by:

$$PV = nRT$$

$$V = n\frac{RT}{P} = \frac{mass(g)}{GFW}\frac{RT}{P}$$

regardless of the nature of the gas

=22.4 L at 1 atm, 273.15ºK

  - Where:
    - P=pressure
    - V=volume
    - n=number of moles
    - T=temp
    - R=universal gas constant=0.08205 L-atm/mole-ºK
    - GFW=gram formula weight

Convert mass to moles

- Now we know that ozone's formula is O_3
  - Which means it contains 3 oxygen atoms
  - Therefore the GFW = 3x atomic weight of oxygen in grams or 48 g/mole

$$\frac{0.056mg \text{ Ozone}}{1m^3 \text{ air}}$$

- n=mass(g)/GFW
- n=0.056x10⁻³g/(48 g/mole)
- n=0.00117x10⁻³ moles

$$\frac{0.00117x10^{-3} moles \text{ Ozone}}{1m^3 \text{ air}}$$

Now determine ppm$_v$

$$ppm_v = \frac{volume_{ozone}}{volume_{air}}$$

$$= \frac{0.00117x10^{-3} moles\ x22.4L/mole}{1m^3 \text{ air}}$$

$$= \frac{0.026x10^{-3} \text{ L Ozone}}{1x10^3 \text{ L air}}$$

$$= 0.026 \text{ ppm}_v \text{ } O_3 \text{ in air}$$

$$= 26 \text{ ppb}_v \text{ } O_3 \text{ in air}$$

Mole & volume fractions

$$\frac{V_i = n_i \frac{RT}{P}}{V_{total} = n_{total} \frac{RT}{P}}$$

- Based on the ideal gas law:
  - The volume fraction (ratio of a component gas volume to the total volume) is the same as the mole fraction of that component
  - Therefore:

$$\frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$$

Defined as: Volume fraction ($\frac{V_i}{V_{total}}$)

Defined as: mole fraction ($\frac{n_i}{n_{total}}$)

  - And since the fraction of the total is one-millionth of the number of ppm:

$$10^{-6}\, ppm_v \equiv \frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$$

Partial pressures

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

- Based on the ideal gas law:
  - And defining the partial pressure (P_i) as the pressure a component gas (i) would exert if all of the other component gases were removed.
  - We can write: $P_i = \frac{n_i}{V_{total}} RT$ and $P_{total} = \frac{n_{total}}{V_{total}} RT$
  - Which leads to: $\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$
  - And: $P_i = P_{total} \frac{n_i}{n_{total}} = P_{total} 10^{-6}\, ppm_v$

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Earth's Atmosphere

Divide by 100 and you get the partial pressure for a total pressure of 1 atm.

Table 2-2. Composition of the Atmosphere*

Compound	Concentration (% volume or moles)	Concentration (ppm_V)
Nitrogen (N_2)	78.1	781,000
Oxygen (O_2)	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide (CO_2)	0.035	350
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane (CH_4)	0.00017	1.7
Krypton (Kr)	0.00011	1.1
Hydrogen (H_2)	0.00005	0.500
Nitrous oxide (N_2O)	0.000032	0.316
Ozone (O_3)	0.000002	0.020

Data from Graedel and Crutzen, 1993.

*Values represent concentrations in dry air at remote locations.

- To next lecture