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CEE 370 Environmental Engineering Principles

Lecture #4
Environmental Chemistry II: Units of Concentration II, Stoichiometry & Chemistry I

Reading: M&Z: Chapter 2

Other: Davis & Masten, Chapter 2; Mihelcic, Chapt 2

Mass Based Concentration Units

- Solid samples

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

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

$$1mg / kg = 1 ppm_m$$

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

- Liquid samples

Density of Water at 5ºC

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

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

$$= 0.35 \text{ ppm}_\text{m} \text{ Fe in water}$$

Orders of magnitude

- Lower as toxicity increases

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 PFAS
pg/L (picograms/liter) 10^{-12}g/L		Pheromones

Molarity

- One mole of any substance contains 6.02 x 10^{23} (Avogadro's number) elementary chemical units (e.g., molecules).
- It is very convenient to measure concentrations in moles, since reactions conform to the law of definite proportions where integer ratios of reactants are consumed (e.g., 1:1, 1:2, etc.) on both a molecular and molar basis.
- It is calculated by:

$$Molarity = \frac{mass/L}{GFW}$$

- Often use M, mM, µM (molar, millimolar, micromolar)
  - To represent: moles/L, 10^{-3} moles/L, 10^{-6} moles/L

Try examples 2.8 & 2.9, on pg. 48 of Mihelcic & Zimmerman

Normality

- Like molarity, but takes into account the stoichiometric ratios of reactants and products
- Measured in equivalents per liter

$$Normality = \frac{mass/L}{GEW}$$

- And Z is an integer related to the number of exchangeable hydrogen ions, or electrons the chemical has, or its overall charge

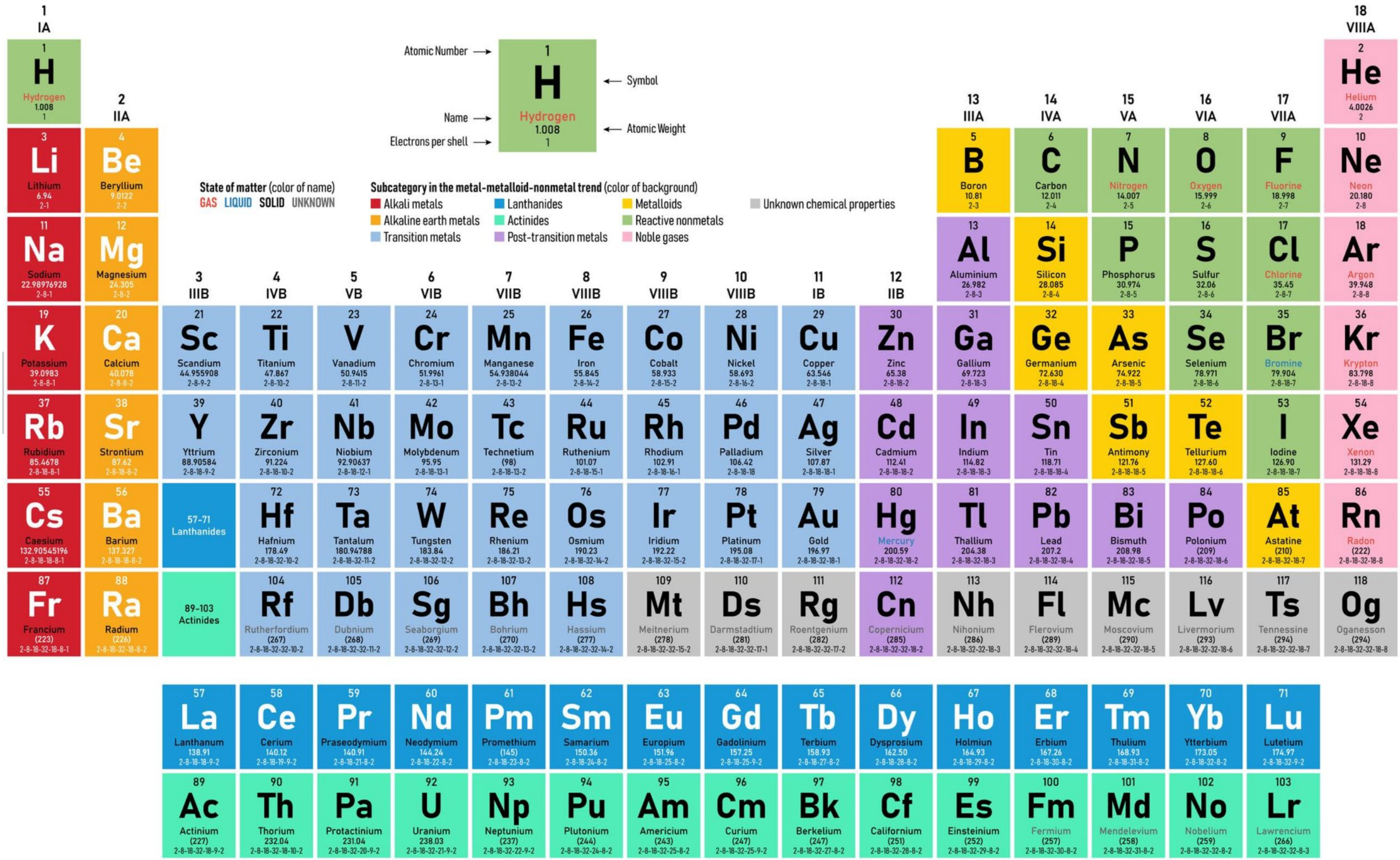
$$GEW = GFW/Z$$

Try examples 2.10-2.11, on pg. 49-50 of Mihelcic & Zimmerman

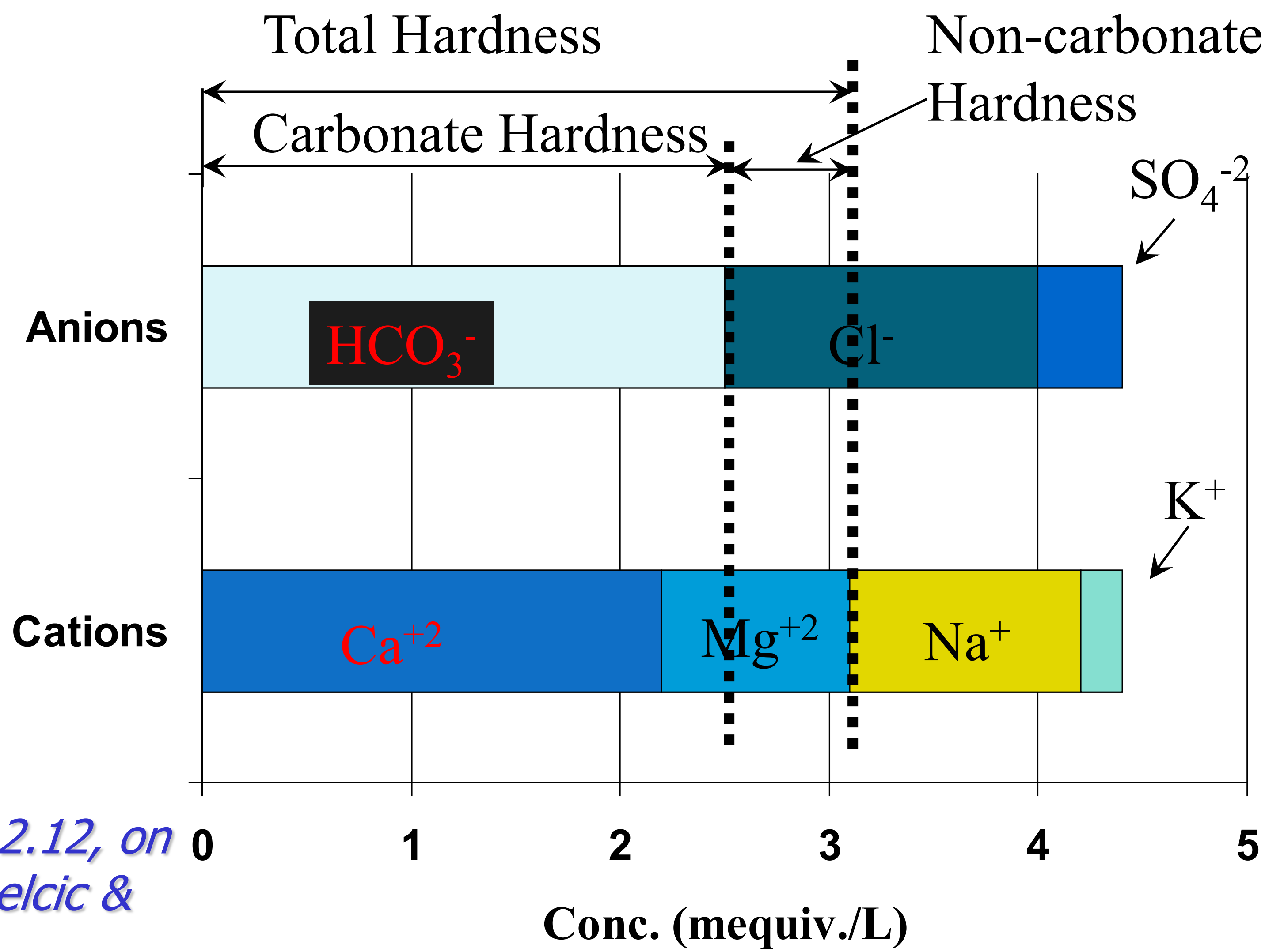
"Complete" water analysis

Species	*mg/L*	*meq/L*
Bicarbonate	153	2.5
Chloride	53	1.5
Sulfate	19.2	0.4
Calcium	44	2.2
Magnesium	10.9	0.9
Sodium	25.3	1.1
Potassium	7.8	0.2

Periodic Table of the Elements



Anion-Cation Balance



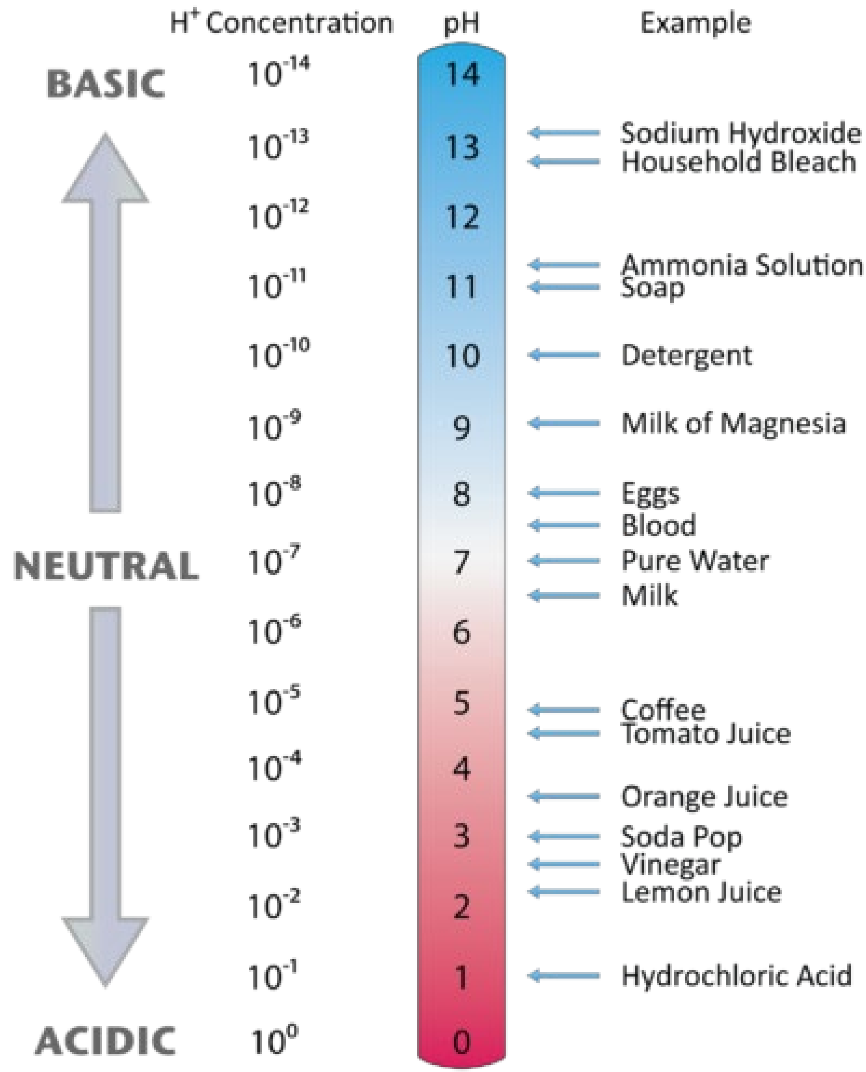
See example 2.12, on pg. 50 of Mihelcic & Zimmerman

pH

- Definition
  - $pH = -\log\{H^+\} \sim -\log[H^+]$
- Significance
  - treatment systems
    - coagulation, softening, ppt of metals, disinfection, biological processes
  - natural systems
    - mineral formation, sorption
  - research

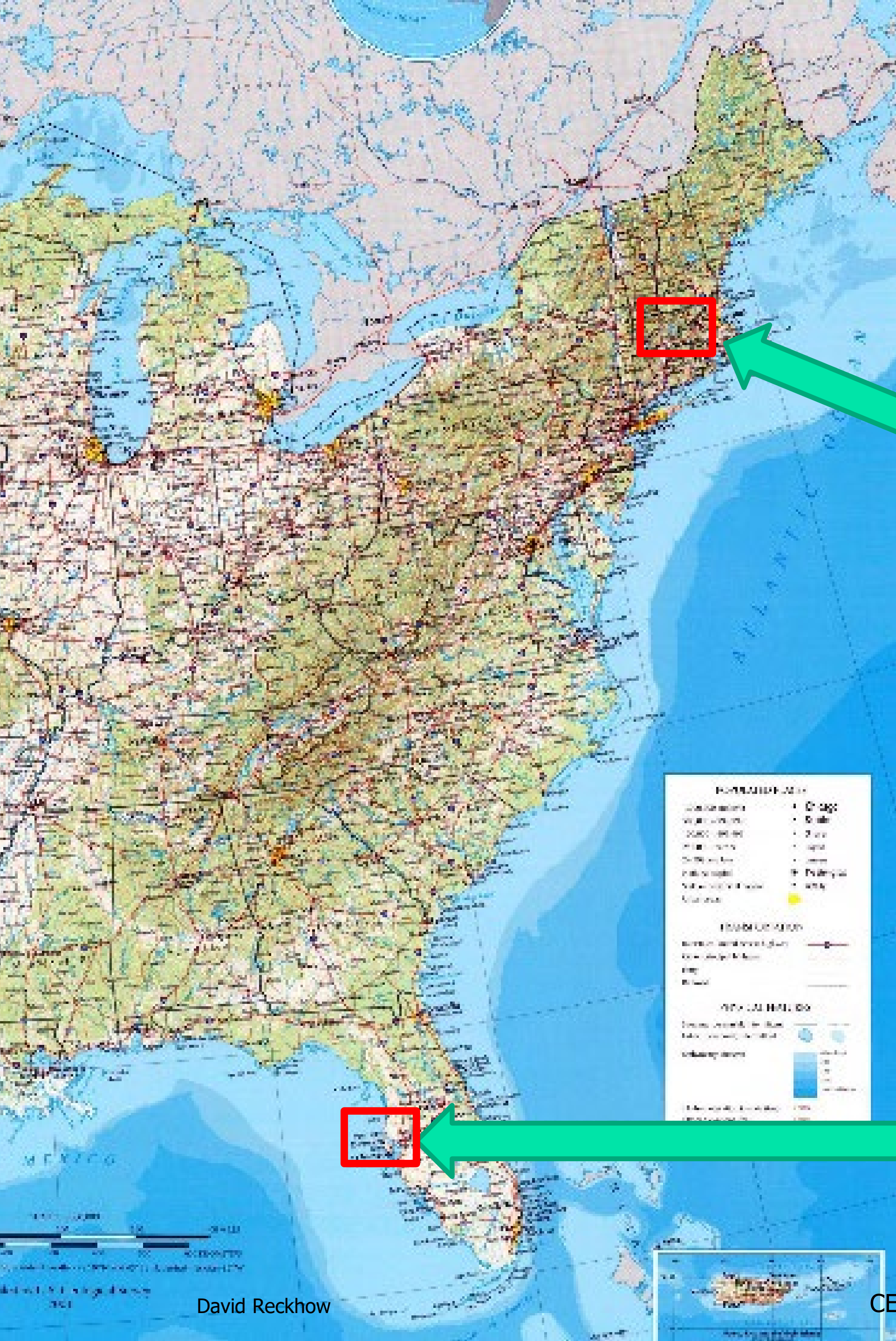
pH

- Where is coke?



https://courses.lumenlearning.com/cheminter/chapter/the-ph-scale/

Example 2: two raw waters



Quabbin Reservoir, MA

- What happens when you add 0.001 moles of HCl to each?

Tampa Bay, FL

Both waters start at pH 7

Tampa Bay, FL

- Alkalinity = 200 mg/L
- pH drops to **6.8**

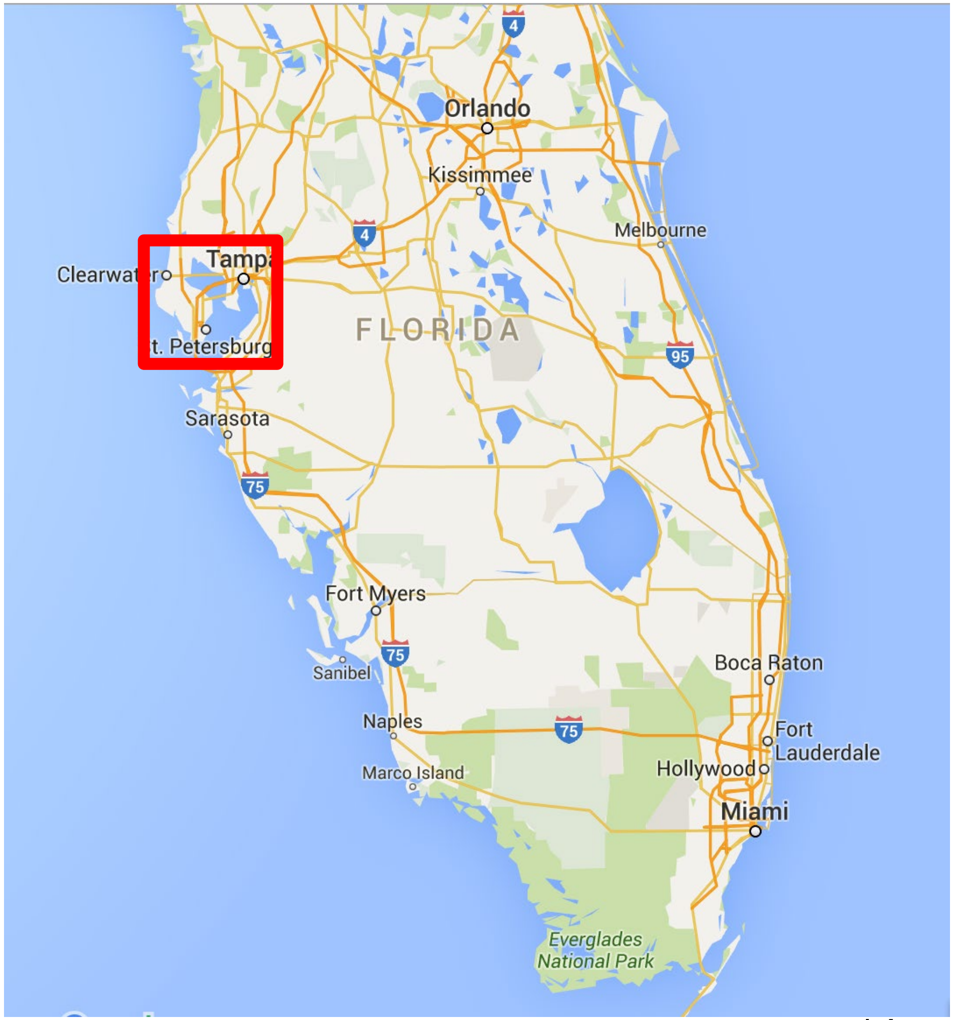
Quabbin Reservoir, MA

- Alkalinity = 5 mg/L
- pH drops to **3.1**

Add 0.001 moles/L of Hydrochloric Acid (HCl) to each

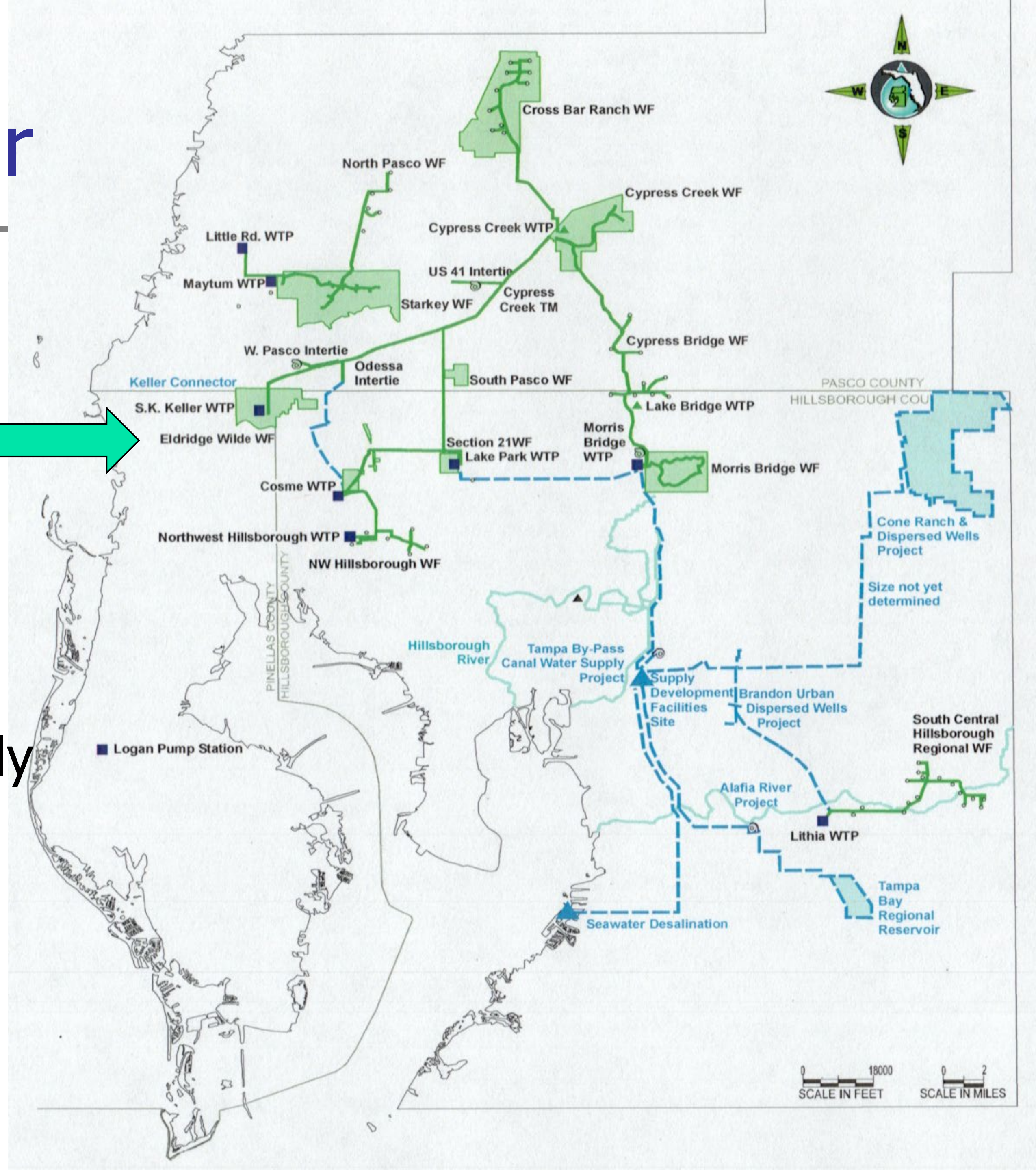
Example 3: differing water quality

- Many, perhaps most, drinking water utilities have multiple sources
- Often those sources have contrasting water quality
- Especially



Groundwater and surface water

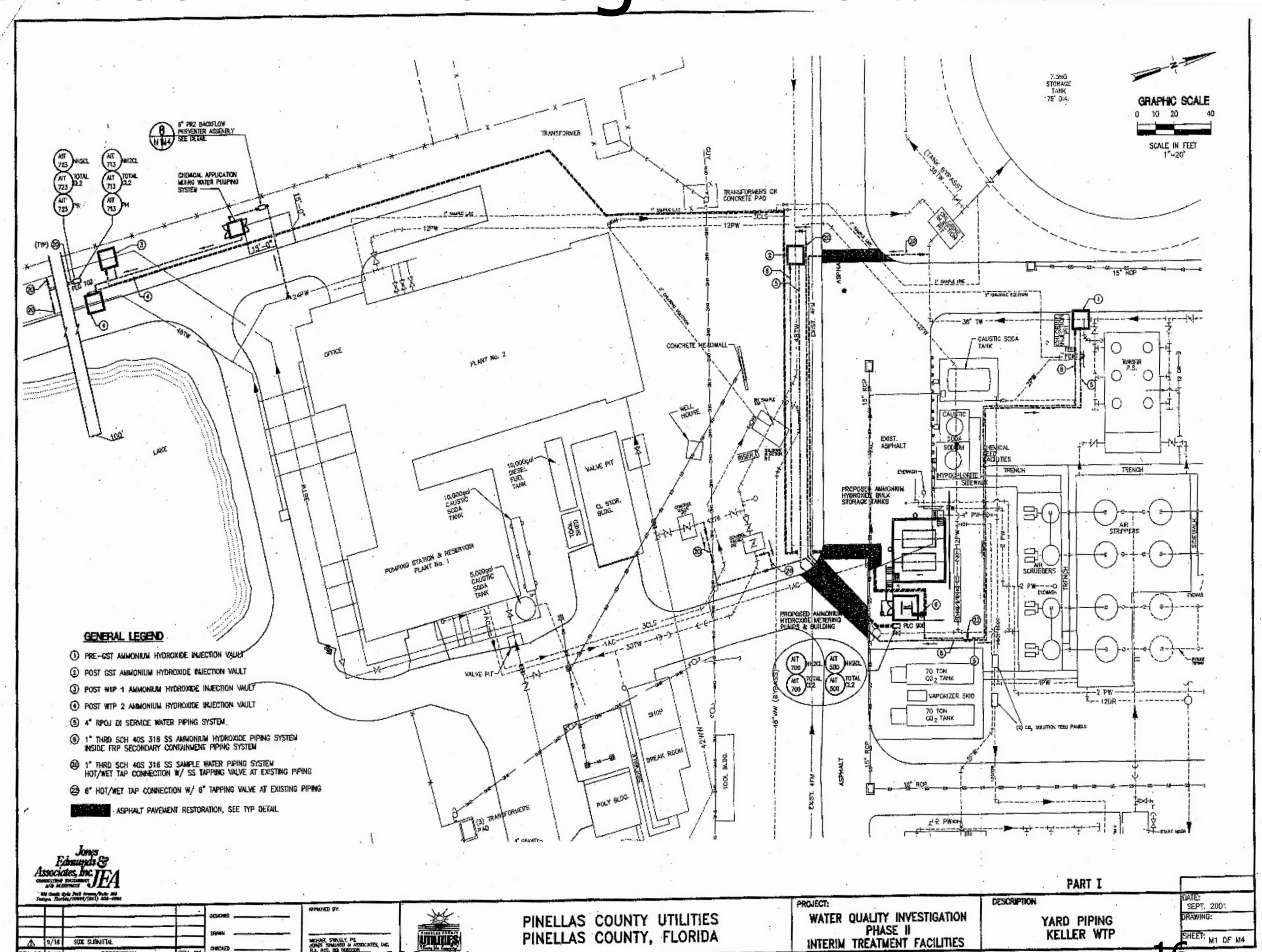
- Tampa Bay area and regional supply
  - Groundwater
  - River water
  - Ocean water: desal



David Reckhow

Keller 2

- Groundwater source: Eldridge Wilde Well field



40 MGD

WQ Challenge
- 1-1.5 ppm H2S, VOCs

Water Treatment
- Air Stripping with CO2
- Chlorination
- Ammoniation
- Polyphosphate

Air treatment
- Water scrubbing with caustic & chlorine

Majors – mostly inorganics

- Keller Plant 2 Sample Station: Aug 9, 2010

Parameter	Value	Units	Parameter	Value	Units
Calcium	77.7	mg/L	Sulfate	4	mg/L
Iron	0.018	mg/L	Phosphorus, Total (as P)	0.23	mg/L
Magnesium	5.08	mg/L	Alkalinity as CaCO3	209	mg/L
Arsenic	0.0002	mg/L	Total Hardness	215	mg/L
Copper	0.0013	mg/L	Total Dissolved Solids	316	mg/L
Lead	0.0001	mg/L	Ammonia as N	0.84	mg/L
Bromide	0.05	mg/L	Free Ammonia as N	0.16	mg/L
Chloride	22	mg/L	Total Organic Carbon	3.7	mg/L
Nitrate as N	0.04	mg/L	UV 254	0.117	cm - 1
Nitrite as N	0.02	mg/L	Heterotrophic Plate Count	3	CFU/ml
Orthophosphate as P	0.12	mg/L	E. coli	1	MPN/100ml
Orthophosphate as PO4	0.37	mg/L	Total Coliforms	1	MPN/100ml

Trace Organics above MDL

- Keller Plant 2 Sample Station: Aug 9, 2010

Parameter	Value	Units	Parameter	Value	Units
Bromodichloromethane	8.3	ug/L	Dibromoacetonitrile	0.77	ug/L
Chloroform	45	ug/L	Dichloroacetonitrile	10.7	ug/L
Dibromochloromethane	0.9	ug/L	Total Haloacetonitriles	13.3	ug/L
Total Trihalomethanes	54.2	ug/L	Trichloroacetonitrile	0.12	ug/L
1,1,1-Trichloro-2-propanone	3.47	ug/L	Chloral hydrate	5.45	ug/L
1,1-Dichloro-2-propanone	1.36	ug/L	Dichloroacetic acid	12.6	ug/L
Bromochloroacetonitrile	1.73	ug/L	Total Haloacetic Acids (HAA5)	31.8	ug/L
Chloropicrin	0.21	ug/L	Trichloroacetic acid	19	ug/L

Tampa Bay Questions

- What does the detailed analysis tell you?
- Does it make sense?
- Expressions of concentration?
- Principle of electroneutrality?
- TDS, TH, Alk, TOC, UV – what do these mean

Tampa Bay water analysis

The major constituents and some microbials

Substance	Conc.	units
Calcium	77.7	mg/L
Iron	0.018	mg/L
Magnesium	5.08	mg/L
Arsenic	0.0002	mg/L
Copper	0.0013	mg/L
Lead	0.0001	mg/L
Bromide	0.05	mg/L
Chloride	22	mg/L
Nitrate as N	0.04	mg/L
Nitrite as N	0.02	mg/L
Orthophosphate as P	0.12	mg/L
Orthophosphate as PO4, calculated	0.37	mg/L
Sulfate	4	mg/L
Phosphorus, Total (as P)	0.23	mg/L
Alkalinity as CaCO3	209	mg/L
Total Hardness	215	mg/L
Total Dissolved Solids	316	mg/L
Ammonia as N	0.84	mg/L
Free Ammonia as N	0.16	mg/L
Total Organic Carbon	3.7	mg/L
UV 254	0.117	cm - 1
Heterotrophic Plate Count	3	CFU/ml
E. coli	1	MPN/100ml
Total Coliforms	1	MPN/100ml

Tampa Bay Calculations

Substance	Conc. (mg/L)	GFW	mM	charge/M	meq/L	pos	neg
Calcium	77.7	40.078	1.9387	2	3.87744	3.87744	
Iron	0.018	55.845	0.0003	3	0.00097	0.00097	
Magnesium	5.08	24.305	0.2090	2	0.41802	0.41802	
Arsenic	0.0002	74.922	0.0000	-1	0.00000		0.00000
Copper	0.0013	63.546	0.0000	2	0.00004	0.00004	
Lead	0.0001	207.2	0.0000	2	0.00000	0.00000	
Bromide	0.05	79.904	0.0006	-1	-0.00063		-0.00063
Chloride	22	35.453	0.6205	-1	-0.62054		-0.62054
Nitrate as N	0.04	14.007	0.0029	-1	-0.00286		-0.00286
Nitrite as N	0.02	14.007	0.0014	-1	-0.00143		-0.00143
Orthophosphate as P	0.12	30.974	0.0039	-3	-0.01162		-0.01162
Orthophosphate as PO4, calculated	0.37	94.97	0.0039	-3	-0.01169		.
Sulfate	4	96.061	0.0416	-2	-0.08328		-0.08328
Phosphorus, Total (as P)	0.23	30.974	0.0074		0.00000		
Alkalinity as CaCO3	209	50.037	4.1769	-1	-4.17691		-4.17691
Total Hardness	215	100.074	2.1484	2	4.29682.		
Total Dissolved Solids	316						
Ammonia as N	0.84	14.007	0.0600.		.		
Free Ammonia as N	0.16	14.007	0.0114	1	0.01142	0.01142	
Total Organic Carbon	3.7	12.011	0.3081		0.00000	0.00000	0.00000
Total =	854.33				sum	**4.30789**	**-4.89726**
	323.33	exclude TDS, TH			diff		-0.58937
					%		12.0%

Tampa Bay Discussion

- Missing Na, K
  - 13.5 mg/L Na would close the balance

Calcium carbonate units

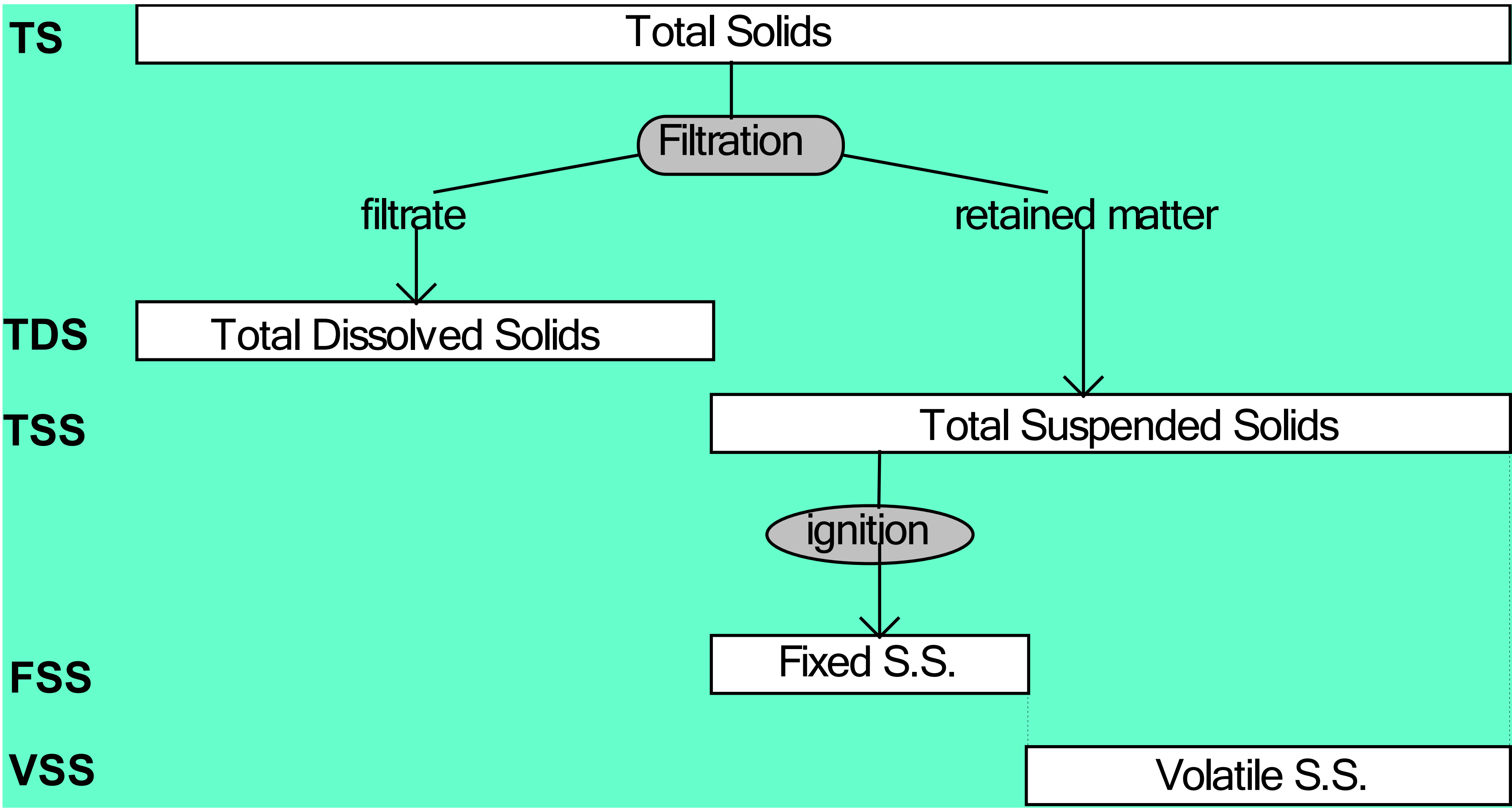
- Used for major ion concentrations in drinking waters
  - Alkalinity
  - Hardness
- Since $CaCO_3$ is divalent (Z=2) and its GFW is 100 g, its GEW is 50 g
  - 50 g/equivalent or 50 mg/meq
  - 50,000 mg/equivalent

See also example 2.14, on pg. 52 of Mihelcic & Zimmerman

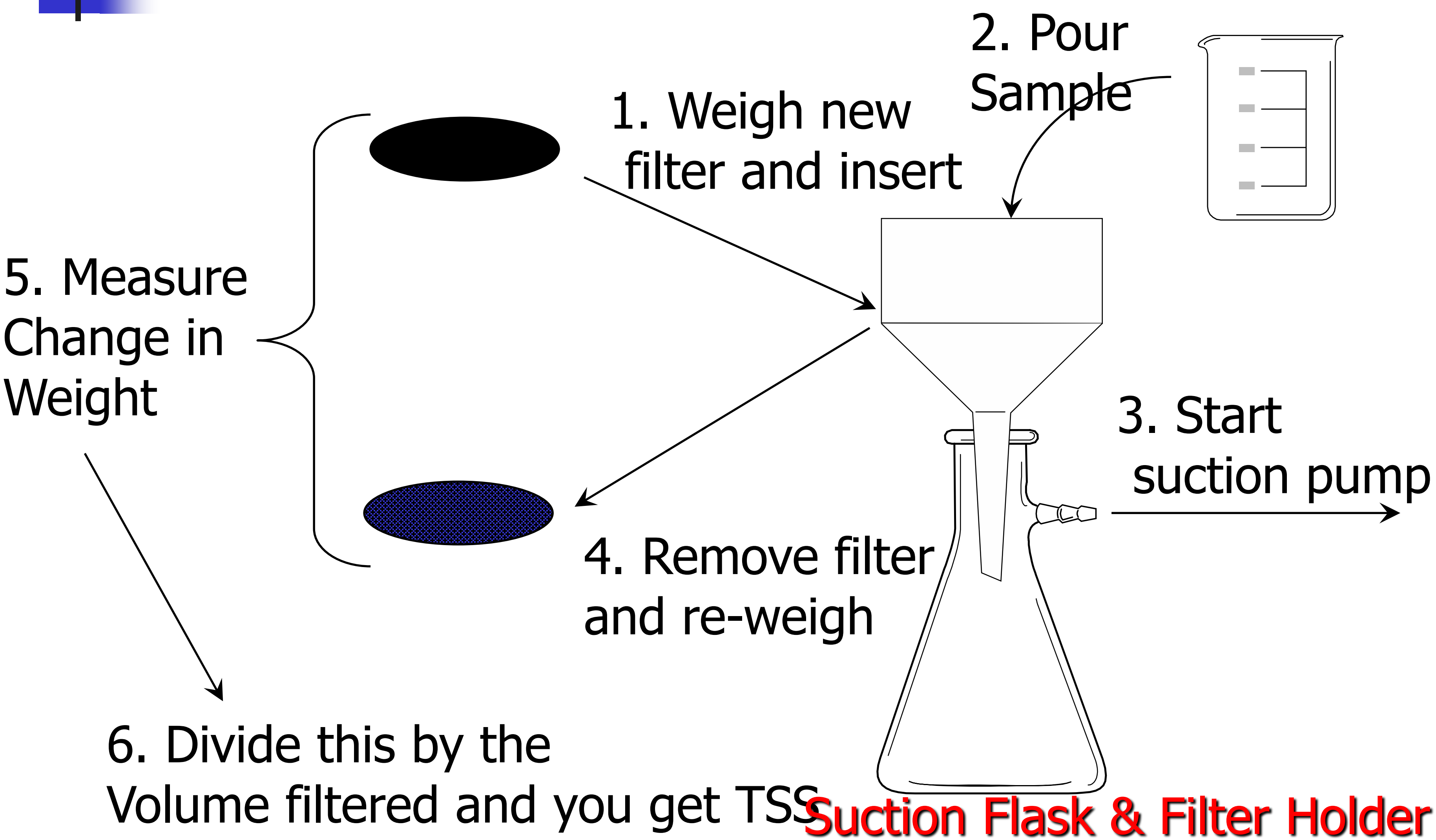
Solids: significance

- TDS: used as a measure of inorganic salt content in drinking waters and natural waters
- TSS: used to assess clarifier performance
- VSS: used to estimate bacterial populations in wastewater treatment systems

Solids Analysis



Filtration for Solids Analysis



- To next lecture