# 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

$$\frac{17.5mg \text{ Pb}}{1kg \text{ soil}} = \frac{17.5x10^{-3} \text{ g Pb}}{1x10^{3} \text{ g soil}} = \frac{17.5g \text{ Pb}}{10^{6} g \text{ soil}} = \frac{17.5g \text{ Pb}}{10^{6} g \text{ soil}}$$
$$= 17.5 \text{ ppm}_{m} \text{ Pb in soil}$$

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



#### Liquid samples

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

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

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

Density of Water at 5°C



## 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)	ppm (parts per million)	Conventional pollutants
$10^{-3}$ g/L		(DO, nitrate, chloride)
μg/L (micrograms/liter)	ppb (parts per billion)	Trihalomethanes, Phenols.
10-6g/L		
ng/L (nanograms/liter)	ppt (parts per trillion)	PCBs, Dioxins
10 <sup>-9</sup> g/L		PFAS
pg/L (picograms/liter)		Pheromones
$10^{-12} g/L$		



- One mole of any substance contains 6.02 x 10<sup>23</sup> (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<sup>-3</sup> moles/L, 10<sup>-6</sup> moles/L

Try examples 2.8 & 2.9, on pg. 48 of Mihelcic & Zimmerman 5



- 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 6



## "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

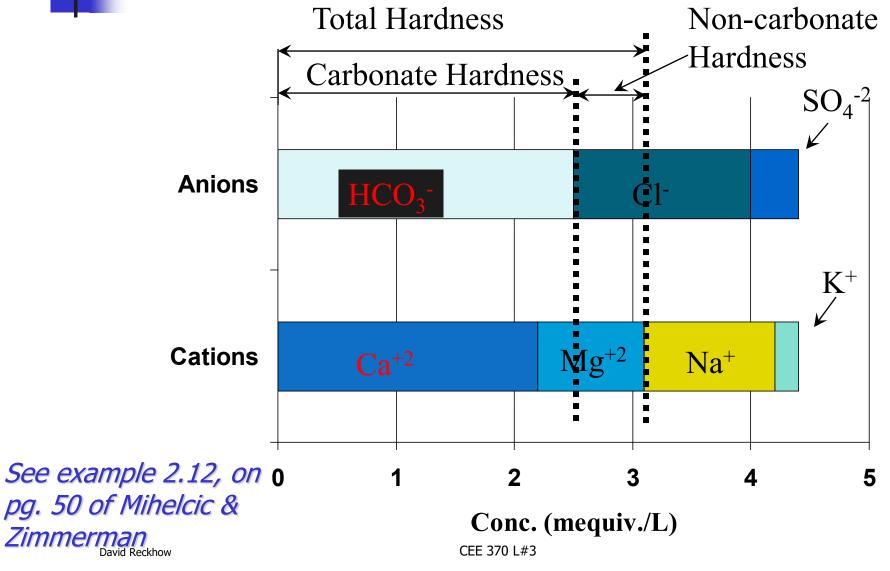
#### Periodic Table of the Elements

1 IA																	18 VIIIA
H					Atomic Number			Sumbol									He
Hydrogen 1.008	2 IIA				Name	→ Hydr	ogen	Symbol Atomic Weight				13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	Helium 4.0026 2
Li	Вe				Electrons per shell		1	Atomic Weight				B	Ć	N	ů	F	Ne
Lithium 6.94 2-1	9.0122 2-2		matter (color of na QUID SOLID UNKN	IOWN A	category in the me lkali metals lkaline earth meta	Lanthani	des	or of background)  Metalloids  Reactive nonm		nown chemical p	roperties	Boron 10.81 2-3	Carbon 12.011 2-4	Nitrogen 14.007 2-5	0xygen 15.999 2-6	Fluorine 18.998 2-7	Neon 20.180 2-8
Na	Mg	3	4	■ T	ransition metals	Post-tran	nsition metals	Noble gases	10	11	12	Al	Si	Phosphorus	Sulfur	Cl	Ar
22.98976928 2-8-1	24.305 2-8-2	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	26.982 2-8-3	28.085 2-8-4	30.974 2-8-5	32.06 2-8-6	35.45 2-8-7	39.948 2-8-8
<b>K</b>	Ca	Sc	Ti	<b>V</b>	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Potassium 39.0983 2-8-8-1	Calcium 40.078 2-8-8-2	Scandium 44.955908 2-8-9-2	Titanium 47.867 2-8-10-2	Vanadium 50.9415 2-8-11-2	Chromium 51.9961 2-8-13-1	Manganese 54.938044 2-8-13-2	Iron 55.845 2-8-14-2	Cobalt 58.933 2-8-15-2	Nickel 58.693 2-8-16-2	Copper 63.546 2-8-18-1	Zinc 65.38 2-8-18-2	Gallium 69.723 2-8-18-3	Germanium 72.630 2-8-18-4	Arsenic 74.922 2-8-18-5	Selenium 78.971 2-8-18-6	Bromine 79.904 2-8-18-7	Krypton 83.798 2-8-18-8
Rb	Sr	39 <b>Y</b>	Zr	Nb	Mo	Tc 43	Ru	Rh	Pd	47 <b>A</b> Cl	Cd	In	Sn	Sb	Te 52	53	Xe
Rubidium 85.4678	Strontium 87.62	Yttrium 88.90584	Zirconium 91.224	Niobium 92.90637	Molybdenum 95.95	Technetium (98) 2-8-18-13-2	Ruthenium 101.07	Rhodium 102.91	Palladium 106.42	Ag Silver 107.87	Cadmium 112.41	Indium 114.82	Tin 118.71	Antimony 121.76	Tellurium 127.60	lodine 126.90	Xenon 131.29
2-8-18-8-1	2-8-18-8-2 <b>56</b>	2-8-18-9-2	2-8-18-10-2 <b>72</b>	2-8-18-12-1 <b>73</b>	2-8-18-13-1 <b>74</b>	75	2-8-18-15-1 <b>76</b>	2-8-18-16-1 <b>77</b>	2-8-18-18	2-8-18-18-1 <b>79</b>	2-8-18-18-2	2-8-18-18-3	2-8-18-18-4	2-8-18-18-5	2-8-18-18-6	2-8-18-18-7	2-8-18-18-8
Cs	Ba	57-71 Lanthanides	Hf Hafnium	Ta	W Tungsten	Re	0s Osmium	Iridium	Pt	Au	Hg	TL Thallium	Pb	Bi	Po	At	Rn
132.90545196 2-8-18-18-8-1	137.327 2-8-18-18-8-2 88		178.49 2-8-18-32-10-2	180.94788 2-8-18-32-11-2	Tungsten 183.84 2-8-18-32-12-2	186.21 2-8-18-32-13-2 107	190.23 2-8-18-32-14-2 108	192.22 2-8-18-32-15-2 109	195.08 2-8-18-32-17-1	196.97 2-8-18-32-18-1	200.59 2-8-18-32-18-2 112	204.38 2-8-18-32-18-3	207.2 2-8-18-32-18-4 114	208.98 2-8-18-32-18-5	(209) 2-8-18-32-18-6	(210) 2-8-18-32-18-7	(222) 2-8-18-32-18-8
Fr	Ra	89-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Ν̈́h	۴l	Мс	LV	Ts	Og
Francium (223) 2-8-18-32-18-8-1	Radium (226) 2-8-18-32-18-8-2	Actinides	Rutherfordium (267) 2-8-18-32-32-10-2	Dubnium (268) 2-8-18-32-32-11-2	Seaborgium (269) 2-8-18-32-32-12-2	Bohrium (270) 2-8-18-32-32-13-2	Hassium (277) 2-8-18-32-32-14-2	Meitnerium (278) 2-8-18-32-32-15-2	Darmstadtium (281) 2-8-18-32-32-17-1	Roentgenium (282) 2-8-18-32-32-17-2	Copernicium (285) 2-8-18-32-32-18-2	Nihonium (286) 2-8-18-32-32-18-3	Flerovium (289) 2-8-18-32-32-18-4	Moscovium (290) 2-8-18-32-32-18-5	Livermorium (293) 2-8-18-32-32-18-6	Tennessine (294) 2-8-18-32-32-18-7	Oganesson (294) 2-8-18-32-32-18-8
			50		40		10	(0		15		45		(0	20		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Τ̈́b	Ďу	Ho	Er	Tm	Yb	Lu	
		Lanthanum 138.91 2-8-18-18-9-2	Cerium 140.12 2-8-18-19-9-2	Praseodymium 140.91 2-8-18-21-8-2	Neodymium 144.24 2-8-18-22-8-2	Promethium (145) 2-8-18-23-8-2	Samarium 150.36 2-8-18-24-8-2	Europium 151.96 2-8-18-25-8-2	Gadolinium 157.25 2-8-18-25-9-2	Terbium 158.93 2-8-18-27-8-2	Dysprosium 162.50 2-8-18-28-8-2	Holmiun 164.93 2-8-18-29-8-2	Erbium 167.26 2-8-18-30-8-2	Thulium 168.93 2-8-18-31-8-2	Ytterbium 173.05 2-8-18-32-8-2	Lutetium 174.97 2-8-18-32-9-2	
		Ac	Th	Pa	92 <b>U</b>	Np	Pu	Am	Cm	Bk	Cf 98	Ës	Fm	Md	No	Lr	

Uranium 238.03 2-8-18-32-21-9-2

## 4

#### **Anion-Cation Balance**

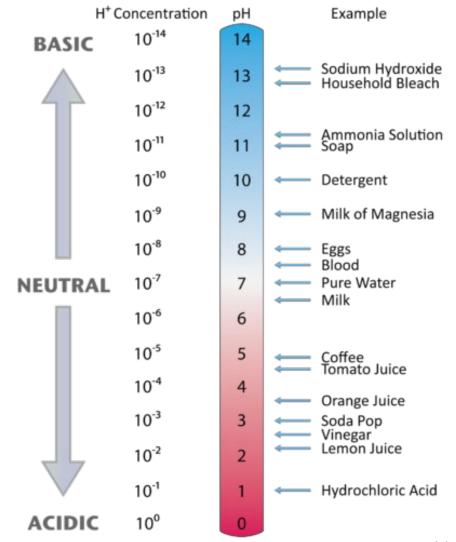


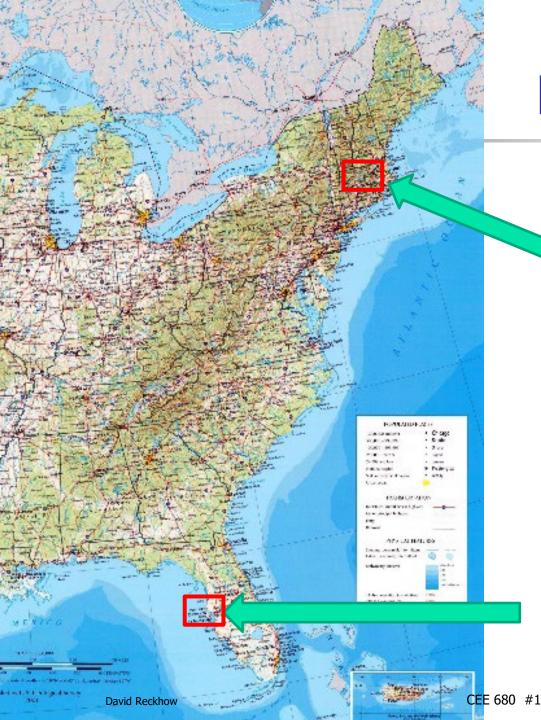


- Definition
  - pH =  $-\log\{H^+\} \sim -\log[H^+]$
- Significance
  - treatment systems
    - coagulation, softening, ppt of metals, disinfection, biological processes
  - natural systems
    - mineral formation, sorption
  - research



Where is coke?





# Example 2: two raw waters

## **Quabbin Reservoir, MA**

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

Tampa Bay, FL



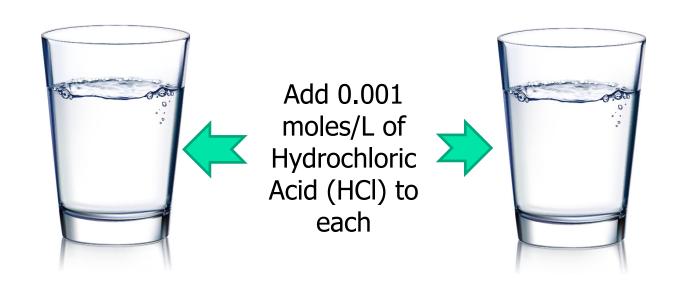
#### Both waters start at pH 7

#### Tampa Bay, FL

- Alkalinity = 200 mg/L
- pH drops to <u>6.8</u>

#### **Quabbin Reservoir, MA**

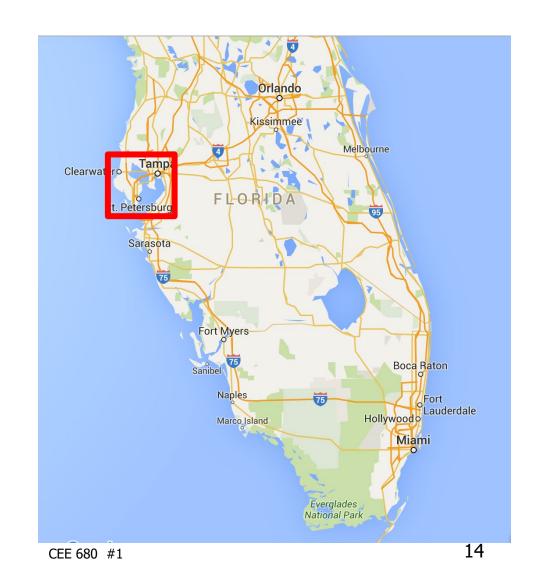
- Alkalinity = 5 mg/L
- pH drops to <u>3.1</u>





#### Example 3: differing water quality

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



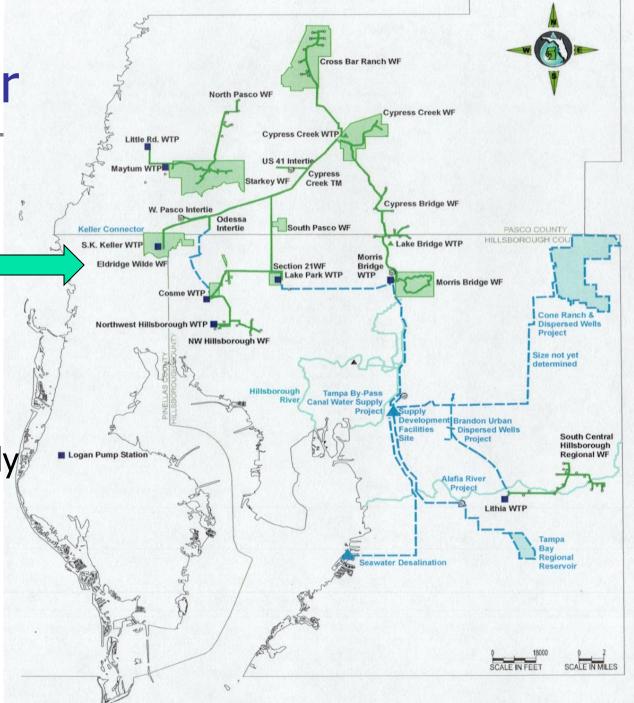
Groundwater and surface water

Tampa Bay area and regional supply

Groundwater

River water

Ocean water: desal





Groundwater source: Eldridge Wilde Well

field

40 MGD WQ Challenge

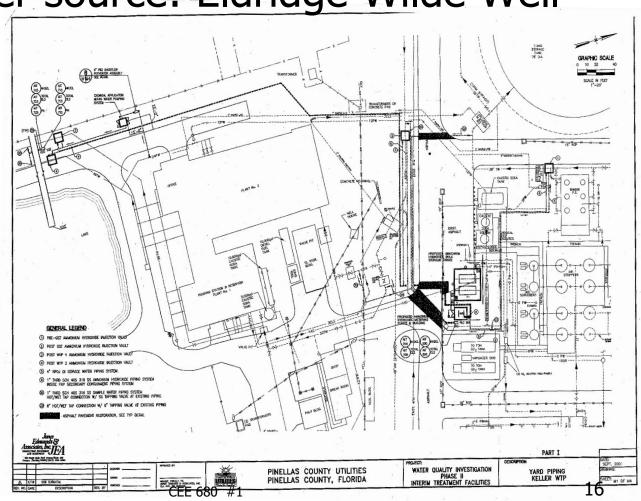
• 1-1.5 ppm H2S, VOCs

#### 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	Smg/L
Magnesium	5.08	lmg/L
Arsenic	0.0002	mg/L
Copper	0.0013	lmg/L
Lead	0.0001	mg/L
Bromide	0.05	img/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,	0.0-	.ma/l
calculated	0.37	,mg/L
Sulfate	4	mg/L
Phosphorus, Total (as P)	0.23	lmg/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

	Conc.						
<u>Substance</u>	(mg/L)	<u>GFW</u>	<u>mM</u>	<u>charge/M</u>	meq/L	<u>pos</u>	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			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			-3 -2	0.0==00		-0.08328
Phosphorus, Total (as P)	0.23				0.00000		-0.00320
Alkalinity as CaCO3	209						-4.17691
Total Hardness	215			2			- <del>4</del> .17091
Total Dissolved Solids	316		2.1707	2	7.29002		
Ammonia as N	0.84		0.0600				
Free Ammonia as N	0.16				0.01142	0.01142	
Total Organic Carbon	3.7	12.011		1	0.00000		
Total =	854.33	12.011	0.3061			<b>4.30789</b>	
iotai –		exclude TD	C TH		sum diff	4.30/09	-0.58937
	323.33	exclude 1D	3, 111		%		12.0%
					70		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<sub>3</sub> 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

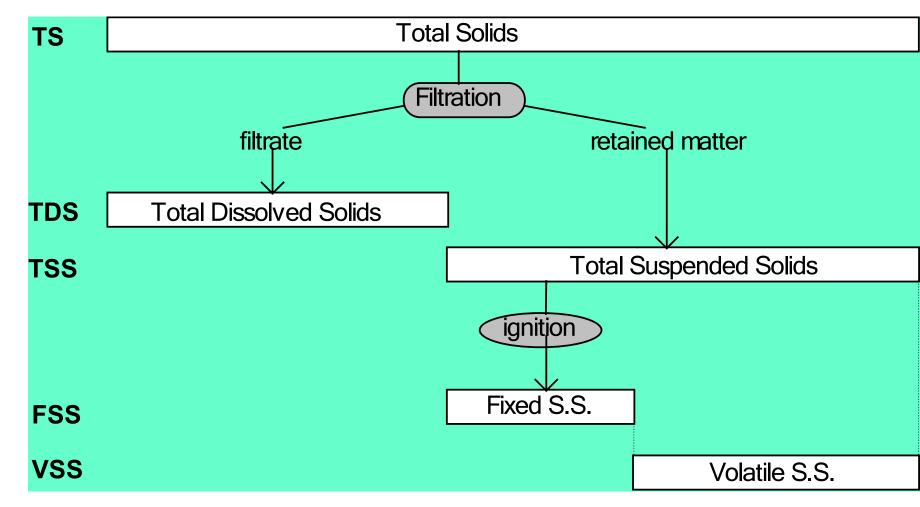


#### Solids: significance

- 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

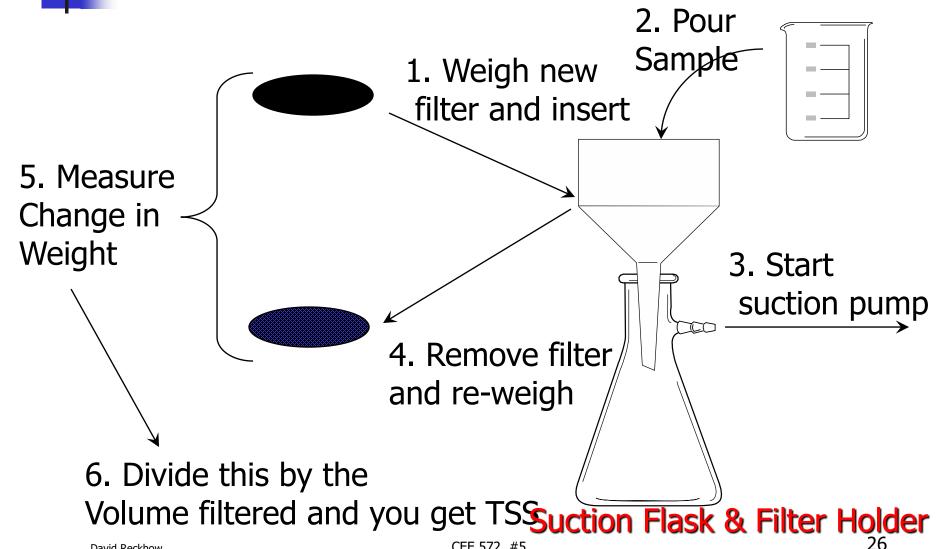


## Solids Analysis



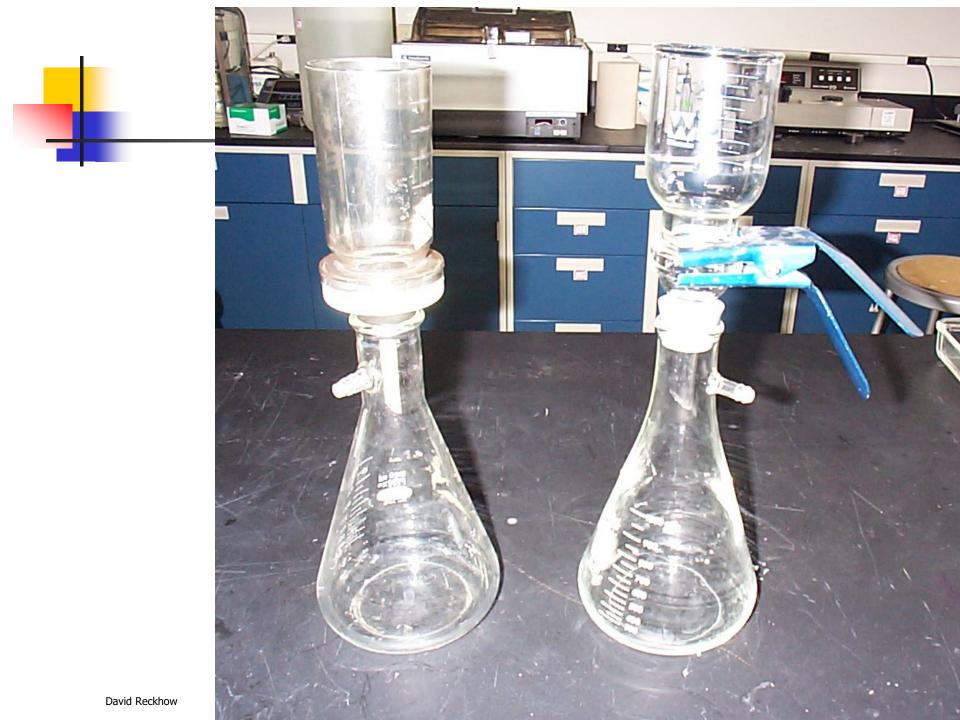


#### Filtration for Solids Analysis



CEE 572 #5 David Reckhow







#### To next lecture