

Groundwater Chemistry and Water Quality

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Groundwater Analysis

- It is not feasible (or sensible) to attempt to measure all possible constituents present in groundwater's.
- A “routine” analysis involves measuring a standard set of constituents.
- The “routine” analysis forms the basis for assessing the suitability of the water for human consumption or various agricultural and industrial uses.

Major Constituents (> 5 mg/L)

- Calcium
- Magnesium
- Sodium
- Bicarbonate
- Chloride
- Sulphate
- pH
- Alkalinity
- TDS
- Conductivity
- Total Hardness
- Silicon
- Carbonic Acid

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Other Reported Results

- **pH** is routinely recorded that measures the hydrogen ion concentration ($-\log[H^+]$).
- **Conductivity** (electrical) is routinely measured in $\mu\text{S/m}$ ($\text{TDS} \approx 0.66 E_c$).
- **TDS** is the total dissolved solids measured as the residue on evaporation.
- **Total alkalinity** (expressed as mg/L CaCO_3) measures the acid-neutralizing capacity of a water sample. It is an aggregate property, primarily due to the carbonate, bicarbonate, and hydroxide content.
- **Total hardness** (expressed as mg/L CaCO_3) is another aggregate property of a water sample. Hardness measures the concentration of multivalent cations, particularly calcium and magnesium.

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Minor Constituents (0.01 to 10 mg/L)

- Potassium
- Iron
- Ammonium
- Carbonate
- Fluoride
- Bromide
- Nitrate/Nitrite

- Carbon Dioxide
- Oxygen
- Boron
- Strontium

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Trace Constituents (< 100 µg/L)

- Li 3
- Be 4
- Al 13
- Sc 21
- Ti 22
- Cr 24
- Mn 25
- Co 27
- Ni 28
- Cu 29

- Zn 30
- Ga 31
- Ge 32
- As 33
- Se 34
- Rb 37
- Yt 39
- Zr 40
- Nb 41
- Mo 42

- Ru 44
- Ag 47
- Cd 48
- In 49
- Sn 50
- Sb 51
- Cs 55
- Ba 56
- La 57
- Ce 58

- W 74
- Pt 78
- Au 79
- Tl 81
- Pb 82
- Bi 83
- Ra 88
- Th 90
- U 92
- Iodide
- Phosphate

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Organic Constituents

- Humic acid
- Fulvic Acid
- Carbohydrates
- Amino Acids
- Tannins
- Lignins
- Hydrocarbons
- Acetate
- Propionate

Typically concentrations are very low

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Routine Analysis

- A “routine” analysis usually includes all the major constituents (except carbonic acid).
- All the minor constituents (except B and Sr that tend to be regarded as trace constituents) are also to be expected.

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Example Routine Analysis

	mg/L		mg/L
• Calcium	<1	• Sulphate	59
• Magnesium	<1	• Bicarbonate	1315
• Sodium	550	• Chloride	45
• Potassium	3.5	• Fluoride	0.25
• Iron	8.7	• Nitrite/Nitrate	<0.1
• Total Hardness	8	• Total Alkalinity	1078
		• TDS	1321
<hr/>			
• pH	7.7		
• Conductivity ⁺	2300 μS/m	• Balance*	1.01

Charge Balance

	mg/L	meq/L		mg/L	meq/L
• Calcium	<1	<0.05	• Sulphate	59	1.22
• Magnesium	<1	<0.08	• Bicarbonate	1315	21.6
• Sodium	550	23.9	• Chloride	45	1.27
• Potassium	3.5	0.09	• Fluoride	0.25	0.01
• Iron	8.7	0.31	• Nitrite/Nitrate	<0.1	>0.01
• Total		24.4	• Total		24.1
<hr/>					
• Molarity	0.0477 M		• Cations/Anions	1.01	

Errors in Analysis

- Checking the ion balance is good practice to eliminate gross errors
- Errors mainly arise as a result of:
 - failure to measure rapidly changing parameters in the field (pH, alkalinity, etc)
 - poor or no filtration (removal of suspended solids)
 - improper sample storage (pressure, temperature, buffering, sealing)

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Specialized Analysis

- Additional specialized measurements are sometimes required for specific projects including:
 - trace metals
 - nutrients (mainly N and P species)
 - organics (mainly hydrocarbons, chlorinated hc's)
 - stable isotopes (^{14}C , ^{18}O , ^2H etc)
 - radionuclides (^{226}Ra , ^{207}Pb , ^{208}Po , ^{231}Th etc)
- Such analyses (listed above in order of increasing cost) can be very expensive and QA/QC is a significant concern.

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You received the data for your sample from the laboratory.

Solutes	Measured Conc. (mg/L)
Ca ²⁺	92.0
Mg ²⁺	34.0
Na ⁺	8.2
K ⁺	1.4
Fe(III)	0.1
HCO ₃ ⁻	325.0
SO ₄ ²⁻	84.0
Cl ⁻	9.6
NO ₃ ⁻	13.0

Sample #3
~ near bridge
pH = 9
TDS = 639
Temp = 50F

Total Dissolved Solids

Fresh waters - (TDS < 1,000 mg/L)
Saline waters - (TDS ~ 35,000 mg/L)

Major Ions : Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻/CO₃²⁻, SO₄²⁻, Cl⁻, NO₃⁻ (conc. > 1mg/L)
Minor Ions : Fe, Mn, Al, Ba, Cd, Co, Cu, Pb, Hg, etc (conc. < 1mg/L)

How do we check correctness of analyses?

Solutes	Measured Conc. (mg/L)
Ca ²⁺	92.0
Mg ²⁺	34.0
Na ⁺	8.2
K ⁺	1.4
Fe(III)	0.1
HCO ₃ ⁻	325.0
SO ₄ ²⁻	84.0
Cl ⁻	9.6
NO ₃ ⁻	13.0
TDS	

1. Check TDS
Measured TDS = Calculated TDS
 $1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$
The measured total dissolved solids concentration should be higher than the calculated one because a significant contributor may not be included in the calculation.
If the ratio is out of the range, constituents should be reanalyzed.

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How do we check correctness of analyses?

2. Check Anion-Cation Balance

The solution must be electrically balanced.

Solutes	Measured Conc. (mg/L)	Atomic weight(g)	Molarity (mmol/L)	Valence (charge)	meq/L
Ca ²⁺	92.0				
Mg ²⁺	34.0				
Na ⁺	8.2				
K ⁺	1.4				
Fe(III)	0.1				
HCO ₃ ⁻	325.0				
SO ₄ ²⁻	84.0				
Cl ⁻	9.6				
NO ₃ ⁻	13.0				

$\sum \text{cations} = \sum \text{anions}$

$\% \text{ difference} = 100 \times \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}}$

Less than 5% ~ reasonable

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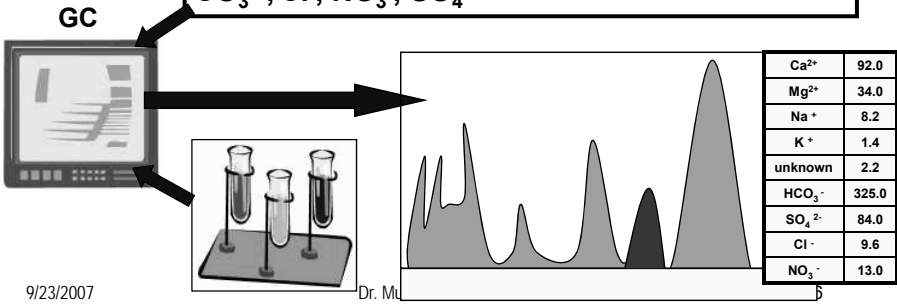
What if there is an electrical imbalance?

Possible reasons:

1. The design of the sampling program neglected a major dissolved species - An important anion or cation was not included in the analysis. Sometimes this can point out the presence of a high concentration of an unusual anion or cation.

Standard Solution : Ca²⁺, Mg²⁺, K⁺, Na⁺, HCO₃⁻, CO₃²⁻, Cl⁻, NO₃⁻, SO₄²⁻

GC



Ca ²⁺	92.0
Mg ²⁺	34.0
Na ⁺	8.2
K ⁺	1.4
unknown	2.2
HCO ₃ ⁻	325.0
SO ₄ ²⁻	84.0
Cl ⁻	9.6
NO ₃ ⁻	13.0

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What if there is an electrical imbalance?

Possible reasons:

2. **Laboratory error - A serious, systematic error has occurred in the analysis.**
3. **Using unfiltered water samples that contain particulate matter that dissolves in the sample when acid is added for preservation purposes.**
4. **The precipitation of a mineral in the sample container that removes the constituents of the mineral from the water.**
5. **In certain cases the dissolved species of the element of compound may not correspond to the typical species used in making the ion balance calculation.**

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WATER QUALITY ASSESSMENT

- **Water quality is determined by assessing three classes of attributes: biological, chemical, and physical.**
- **The national standards for drinking water are developed by Environmental Protection Agency (EPA) and WHO.**
- **The EPA drinking water standards are categorized as primary drinking water standards and secondary drinking water standards.**
 - **Primary drinking water standards - organic and inorganic chemicals, microbial pathogens, and radioactive elements**
⇒ **affect the safety of drinking water**
 - **Secondary drinking water standards - chloride, color, copper, corrosivity, foaming agents, iron, manganese, odor, pH, sulfates, total dissolved solids, and zinc**
⇒ **affect qualities of drinking water like taste, odor, color, and appearance**
- **These standards set a limit - Maximum Contaminant Level (MCL).**

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Calcium (Ca^{2+})

- Most abundant of the alkaline-earth metals.
- Calcium is derived from nearly all rocks (sedimentary, Igneous, metamorphic).
- The greatest concentrations come from calcite (CaCO_3) and gypsum (CaSO_4) .
- Calcite & gypsum are common minerals in sedimentary environments (limestone makes up approximately 10 percent of all sedimentary rock).
- Contributes to hardness

See, 2004, Colorado School of Mines

Magnesium (Mg^{2+})

- Magnesium is found in many minerals, including dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnesite (MgCO_3) and many types of clay.
- Comes from underground deposits of brine.
Sea Water Ion Percentage

Chloride (Cl): 55.04 %	Sodium (Na): 30.61 %
Sulphate (SO_4): 7.68 %	Magnesium (Mg): 3.69 %
Calcium (Ca): 1.16 %	Potassium (K): 1.10 %
- Contributes to hardness

See, 2004, Colorado School of Mines

Sodium (Na^+)

- A major source of Na^+ in natural waters is from the weathering of feldspars, evaporates and clay. It is gradually released from rocks. Concentrations therefore increase with time.
- Na^+ is the second most abundant element dissolved in seawater.
- Na^+ is more mobile in soil than potassium and so it is used often as an indicator of human impacts to shallow ground water.
- Higher levels of Na^+ may be due to contamination by human activities including: use of road de-icing salts, discharges from water softeners, human or animal waste disposal, leachate from landfills and many other activities.

Seo, 2004, Colorado School of Mines

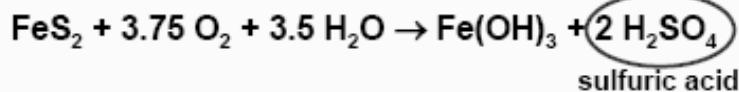
Potassium (K^+)

- K^+ is commonly found in sedimentary rocks and released slowly upon dissolution of rocks (potassium feldspars and mica minerals).
- Consequently, concentrations increase as residence time in groundwater increases.
- K^+ is an important fertilizer and strongly held by clay particles in soil.
- Its presence is of great importance for soil health, plant growth and animal nutrition.
- Sodium and potassium are often associated with chloride and bromide. In these forms, they readily dissolve in water.

Seo, 2004, Colorado School of Mines

Sulfate (SO_4^{-2})

- Gypsum (CaSO_4) is the most important source for sulfate (Gypsum is one of the more common minerals in sedimentary environments).
- High concentrations occur in shallow, unconfined aquifers that receive large inputs of sulfate from atmospheric deposition, fertilizer use and land application of animal wastes.
- Elevated in acid mine drainage areas.



http://www.mines.edu/fs_home/jhoran/ch126/index.htm

See, 2004, Colorado School of Mines

Phosphates (PO_4^{-3})

- Phosphorus is usually present in natural water as phosphates (PO_4^{-3}).
- Factors Affecting Phosphorus Concentrations
 - Wastewater and Septic System Effluent - Organic phosphates are contributed to sewage by body waste and food residues.
 - Detergents & Fertilizers
 - Animal Waste
 - Development/Paved Surfaces - Development can cause soil erosion, which will release phosphorus.
 - Industrial Discharge - Phosphates are often added to water to prevent iron oxides or calcium carbonates from forming.
 - Forest Fires – can cause soil erosion

See, 2004, Colorado School of Mines

Nitrate (NO_3^-)

- Nitrate (NO_3^-) is one of the major ions in natural waters and comes into water through the nitrogen cycle rather than via dissolved minerals.
- High concentrations of NO_3^- is the result of contamination of ground water supplies by septic systems, feed lots, and agricultural fertilizers.
- In aerobic condition, NO_3^- is stable and tends to be conservative in most groundwater environments.

See, 2004, Colorado School of Mines

Bromide (Br^-)

- Bromine is found in sea water and exists as the bromide ion at a level of about 65 mg/l.
- Br is a conservative ion (no water-rock interaction), so Br/Cl ratio is used to trace origins of salinity (eg. For ocean water, $\text{Br/Cl} = 3.5 \times 10^{-3}$).
- Groundwater flowing through aquifer with halite (NaCl)
⇒ Salt dissolution will lower Br/Cl as Cl increases.
- Bromine has been used in swimming pools and cooling towers for disinfection.
- Organic bromines are widely used as sprays to kill insects and other unwanted pests.
- Over 0.05 mg/l in fresh water may indicate the presence of industrial wastes, possibly from the use of pesticides or biocides containing bromine.

See, 2004, Colorado School of Mines

Chloride (Cl^-)

- Chlorine alone as Cl_2 is highly toxic, and it is often used in disinfectants, paper production (bleach), antiseptic, dyestuffs, food, insecticides, paints, petroleum products, plastics, solvents, and many other consumer products.
- Chloride (Cl^-) is a salt compound resulting from the combination of the gas chlorine and a metal (NaCl , MgCl_2) . Almost all chloride salts are highly soluble in water.
- Chlorides may get into surface water from several sources including: rocks containing chlorides, agricultural runoff, wastewater from industries, oil well wastes, and effluent wastewater from wastewater treatment plants.
- Does not substitute for other anions (no water-rock interaction)
⇒ Used in mass balance calculations for mixing of water bodies (conservative element).

See, 2004, Colorado School of Mines

WATER SAMPLING

General Observations: The following information should be recorded when conducting the water sampling tests.

1. Name and location of the river, stream, lake or pond that you are testing.
2. Latitude and longitude of the water source location.
3. Date and time of water sampling.
4. Weather conditions at the time and, if appropriate, recent weather conditions (i.e. day after a big rain storm).
5. Condition of the river, stream, lake or pond. For example, does it appear to be polluted with any debris or matter? Are there any fish or plants in the water? Is there a lot of algae growing in it?
6. Any other observations that you think are interesting or significant.

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PHYSICAL CHARACTERISTICS - 2

- Odors – result from the presence of decaying organic matter or, in the case of mineral springs, the reduction of sulfates to hydrogen sulfide gas (H₂S)
- Offensive odors commonly encountered in water

Compound	Descriptive Quality
Amines	Fishy
Ammonia	Ammoniacal
Diamines	Decayed Flesh
Hydrogen Sulfide	Rotten Egg
Mercaptans	Skunk Secretion
Organic Sulfides	Rotten Cabbage
Skatole	Fecal

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PHYSICAL CHARACTERISTICS - 3

- Temperature should be measured in the field.
- Temp affects a number of water quality parameters.
- When temp increased,
 - Chemical & biochemical reaction rates increase
 - Gas solubility decreases (specially impact on oxygen)
 - Mineral solubility increases
 - Growth rates of aquatic organisms increases
- The equilibrium constants must be recalculated using the temp of the aquifer.

$$\log \frac{K_2}{K_1} = \frac{\Delta H_R^0}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

Where K_2 = equilibrium constant at temp of interest, T_2
 K_1 = equilibrium constant at 25°C, T_1
 ΔH_R^0 = change in the enthalpy of the reaction (cal/mole)
 R = gas constant (1.987 cal/°mole)

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Sedimentation/siltation

- Excessive sedimentation in streams and rivers is considered to be a major cause of surface water pollution in the U.S. by the USEPA



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Measures of sedimentation

- Suspended sediments
- Turbidity
- Embedddness

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High turbidity and suspended solids

- Caused by many factors including:
 - soil erosion
 - domestic and industrial wastewater discharge
 - urban runoff
 - flooding
 - algal growth due to nutrient enrichment
 - dredging operations
 - channelization
 - removal of riparian vegetation and other stream bank disturbances

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Total suspended solids and turbidity

- Both are indicators of the amount of solids suspended in the water
 - Mineral (e.g., soil particles)
 - Organic (e.g., algae, detritus)
- TSS measures the actual weight of material per volume of water (mg/L)
- Turbidity measures the amount of light scattered
- Therefore, TSS allows the determination of an actual concentration or quantity of material while turbidity does not

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Measuring TSS



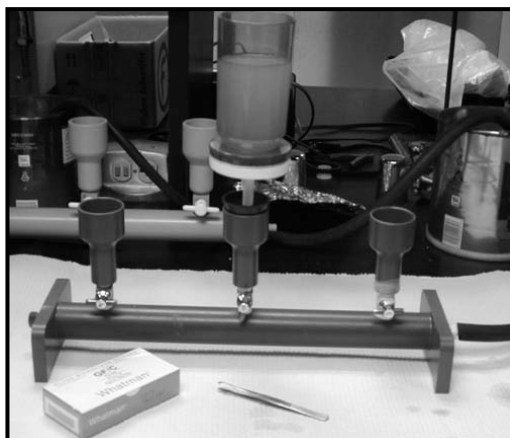
1. Filter a known amount of water through a pre-washed, pre-dried at 103-105 °C, pre-weighed ($\sim \pm 0.5$ mg) filter
2. Rinse, dry and reweigh to calculate TSS in mg/L (ppm)
3. Save filters for other analyses such as volatile suspended solids (VSS) that estimate organic matter

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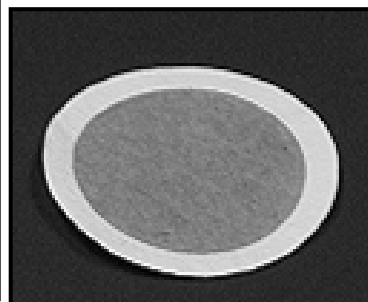
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Total suspended solids - method



What type of filter to use?



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Total suspended solids

Calculate TSS by using the equation below

$$\text{TSS (mg/L)} = ([A-B] \times 1000) / C$$

where

A = final dried weight of the filter (in milligrams = mg)

B = Initial weight of the filter (in milligrams = mg)

C = Volume of water filtered (in Liters)

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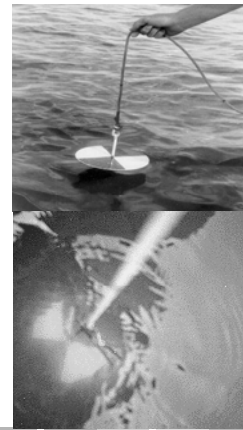
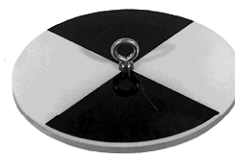
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PHYSICAL CHARACTERISTICS - 1

- Turbidity – the clarity of water (NTUs: nephelometric units)
- This test has little meaning except in relatively clear waters but is very useful in defining drinking-water quality in water treatment.
- The Secchi disk is used to measure how deep a person can see into the water.
- Transparency of lake water is affected by a variety of factors including human activity, decaying plant matter, algal blooms, suspended sediments, and plant nutrients.
- Turbidity provides a cheap estimate of the total suspended solids or sediments (TSS) concentration (in milligrams dry weight/L).

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Measuring turbidity

- Turbidity measures the scattering effect suspended particles have on light
 - inorganics like clay and silt
 - organic material, both fine and colored
 - plankton and other microscopic organisms
- Transparency or turbidity tubes



Even small amounts of wave action can erode exposed lakeshore sediments, in this case a minepit lake from northeastern Minnesota. Guess the mineral mined here.

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Turbidity - Nephelometric optics

- Nephelometric turbidity estimated by the scattering effect suspended particles have on light
- Detector is at 90° from the light source

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Turbidity – units and reporting

- Nephelometric Turbidity Units (NTU)
standards are formazin or other certified material
- JTU's are from an “older” technology in
which a candle flame was viewed through a
tube of water

1 NTU = 1 JTU (Jackson Turbidity Unit)

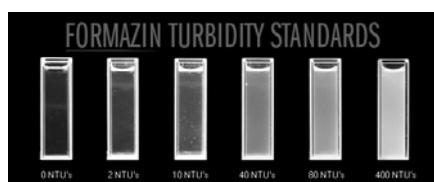
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Turbidity - standards

- Top - a range of
formazin
standards
- Bottom –the
same NTU
range using a
clay suspension



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Water clarity – transparency



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Water clarity – transparency tubes

- **Used in streams, ponds, wetlands, and some coastal zones**
- **Analogous to secchi depth in lakes: a measure of the dissolved and particulate material in the water**



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Water clarity – transparency tubes

- Useful for shallow water or fast moving streams bodies where a secchi would still be visible on the bottom
- It is a good measure of turbidity and suspended sediment (TSS)
- Used in many volunteer stream monitoring programs

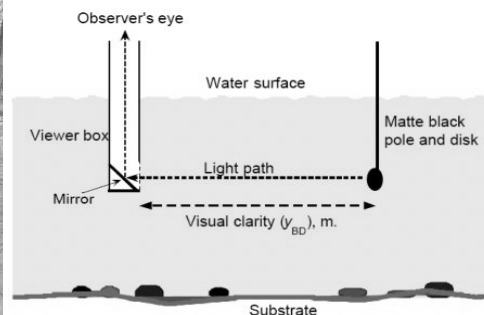
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Horizontal secchi

- Newer method – all-black disk viewed horizontally



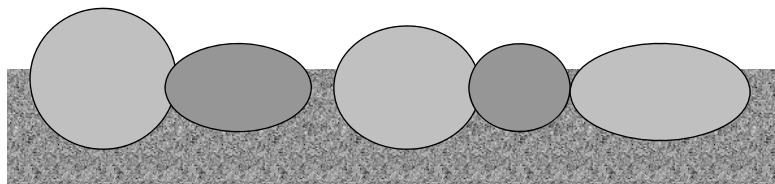
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Embeddedness

- Measure of fine sediment deposition in the interstitial spaces between rocks
- High embeddedness values indicate habitat degradation
- Visual assessment used to estimate the degree of embeddedness



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Embeddedness – cont.

- The stream-bottom sediments to the top right provide spaces for fish to lay eggs and for invertebrates to live and hide.
- Excess erosion has deposited fine grained sediments on the stream bottom to the bottom right. There are no spaces available for fish spawning or for invertebrate habitat.



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Embededdness – visual assessment

- **Embeddedness: General guidelines**
 - 0% = no fine sediments even at base of top layer of gravel/cobble
 - 25% = rocks are half surrounded by sediment
 - 50% = rocks are completely surrounded by sediment but their tops are clean
 - 75% = rocks are completely surrounded by sediment and half covered
 - 100% = rocks are completely covered by sediment

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CHEMICAL CHARACTERISTICS - 1

- Major species - Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^{-} , SO_4^{2-} , Cl^{-} , NO_3^{-}

Constituent	Source
$\text{Ca}(\text{HCO}_3)_2$	Dissolution of limestone, marble, chalk, calcite, dolomite, & other minerals containing CaCO_3
$\text{Mg}(\text{HCO}_3)_2$	Dissolution of magnesite, dolomite, dolomitic limestone, & other minerals containing MgCO_3
$\text{Na}(\text{HCO}_3)_2$	White salt commonly known as baking soda, typically a manufacture product; also present in some natural waters
CaSO_4	Minerals such as gypsum, alabaster, & selenite
MgSO_4	Salt beds or mines as Epsom salt
Na_2SO_4	Salt lakes, salt beds, caverns, etc
CaCl_2	Natural brines, salt beds, etc & by-product of the chemical industry
MgCl_2	Natural brines, salt beds, etc
NaCl	Salt lakes, salt beds, connate water, other natural brine

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CHEMICAL CHARACTERISTICS - 2

- Minor species – derived from the contact of water with various mineral deposits.
 Al^{3+} , NH_4^+ , As^+ , Ba^{2+} , BO_4^{3-} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} ,
 HSO_4^- , HSO_3^- , CO_3^{2-} , F^- , OH^- , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , S^{2-} ,
 SO_3^{2-}
- Inorganic species added by humans
 - As^{3+} , Ba^{2+} , Cd^{2+} , Cr^{3+} , Cr^{6+} , Pb^{2+} , Hg^{2+} , Se , Ag^{2+} , Zn^{2+} , CN^-
 - These constituents are of concern primarily because of their toxicity to microorganisms, plants, and animals.
 - Typically the presence of these constituents is due to the discharge of improperly processed industrial wastes.

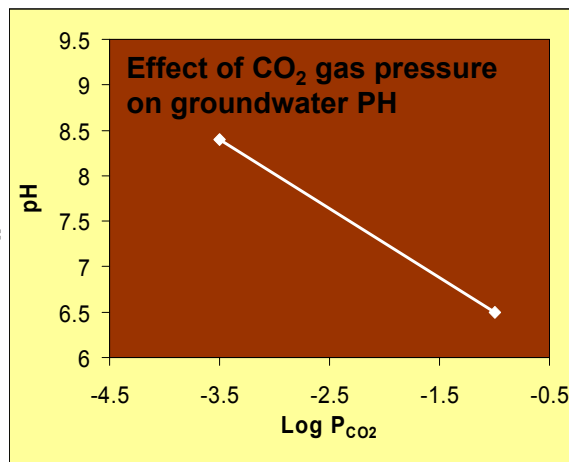
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CHEMICAL CHARACTERISTICS - 3

- pH (Hydrogen Ion Activity) affects aqueous complexation, mineral solubility, adsorption properties, gas solubility, & biochemical reactions.
- A sample of GW ~ originally in equilibrium with calcite at $P_{\text{CO}_2} = 0.1$ atm
 ⇒ allowed to equilibrate with atmosphere ($P_{\text{CO}_2} = 0.0003$ atm)
- Large change in pH (pH 6.5 → 8.4) would have a major effect on the solubility of minerals.

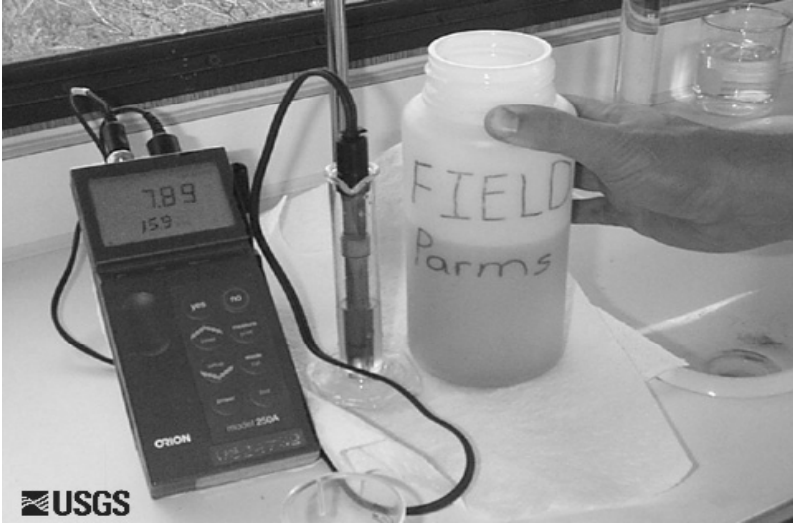


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pH



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pH

- The pH of water determines the solubility (amount that can be dissolved in the water) and biological availability (amount that can be utilized by aquatic life) of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium, etc.).

	14	
bleach	13	
ammonia	12	
	11	
	10	
	9	
	8	sea water
	7	distilled water
	6	pure rain
beer	5	most fish species die
vinegar	4	
lemon juice	3	
	2	
	1	

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pH – importance in aquatic systems

- The pH of a sample of water is a measure of the concentration of hydrogen ions.
- pH determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium, etc.).

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pH - reporting

- pH can be measured electrometrically or colorimetrically (pH paper) BUT ONLY the former technique is approved by the EPA and USGS for natural waters.
- The electrometric method uses a hydrogen ion electrode.
- pH meters require extensive care in handling and operation.
- Report to the nearest 0.1 standard pH unit

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pH – probes

● Field probe types:

- Combination probes (e.g. YSI)
 - Less expensive; more rugged design
 - Less precise
 - Shorter life because reference solution cannot be replenished
- Separate reading and reference electrodes (e.g., Hydrolab)
 - Costs more
 - More precise; faster response time
 - Allows user maintenance; Teflon junction and electrolyte can be replaced

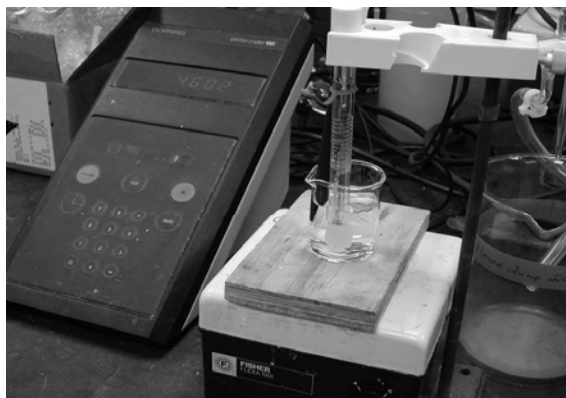
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pH – probes

- Or, alternatively, a bench or hand-held meter and probe can be used in a fresh subsample if you don't have a field meter with a pH probe.



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CHEMICAL CHARACTERISTICS - 4

- **Alkalinity** – to determine the dissolved inorganic carbon concentration ($\text{CO}_2(\text{aq})$, H_2CO_3 , HCO_3^- , CO_3^{2-}) of a water sample
- **Hardness** – to measure the soap-consuming capacity & scale-forming tendency of the water ($\text{Ca}^{2+} + \text{Mg}^{2+}$)
- **Conductivity**
 - measure of electrical current ($\mu\text{S}/\text{cm}$)
 - Because the electrical current is transported by the ions in solution, the conductivity increases as the concentration of ions increases.
 - Conductivity estimates the amount of total dissolved solids (TDS).

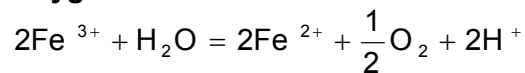
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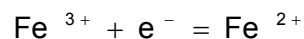
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CHEMICAL CHARACTERISTICS - 5

- **Redox = Oxidation + Reduction**
- **Oxidation** : substance loses or donates electrons (e^-)
- **Reduction** : substance gains or accepts electrons (e^-)
- **Redox reactions** can be thought of as reactions involving transfer of oxygen.



In solution chemistry it is generally more convenient to consider redox reactions as electron transfers.



- **The redox potential** is a measure of the affinity of a substance for electrons.
- **Unit in volts** - a transfer of electrons is an electrical current.

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REDOX POTENTIALS (Eh)

- Redox Potential can be measured using Redox tester on site.



- Redox Potential (Eh) by the Nernst equation:

$$Eh = E^0 + \frac{RT}{nF} \ln K_{sp} \quad Eh = E^0 - \frac{0.0592}{1} \log \frac{p_{H_2}^{1/2}}{a_{H^+}}$$

where E^0 = standard potential (at 25°C & 1 atm pressure)

R = gas constant (kcal/(mol•K))

T = temperature (kelvins)

F = Faraday constant (23.1 kcal/V)

n = number of electrons

K_{sp} = solubility product

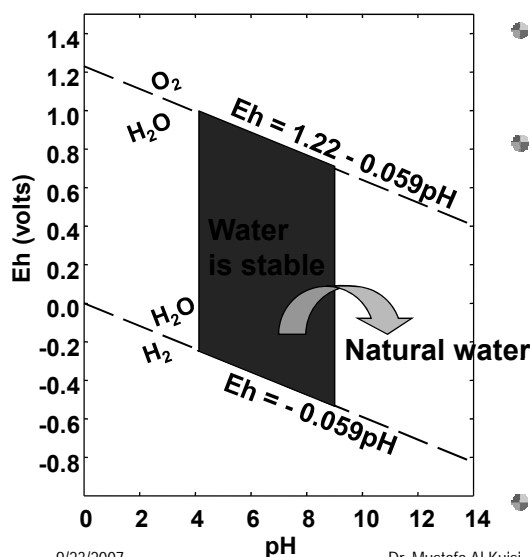
$$(\log K_{sp} = \frac{-\Delta_r G^0}{2.303RT})$$

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Eh-pH DIAGRAM



- This diagram shows the stability limits of water at 25°C and 1 bar.

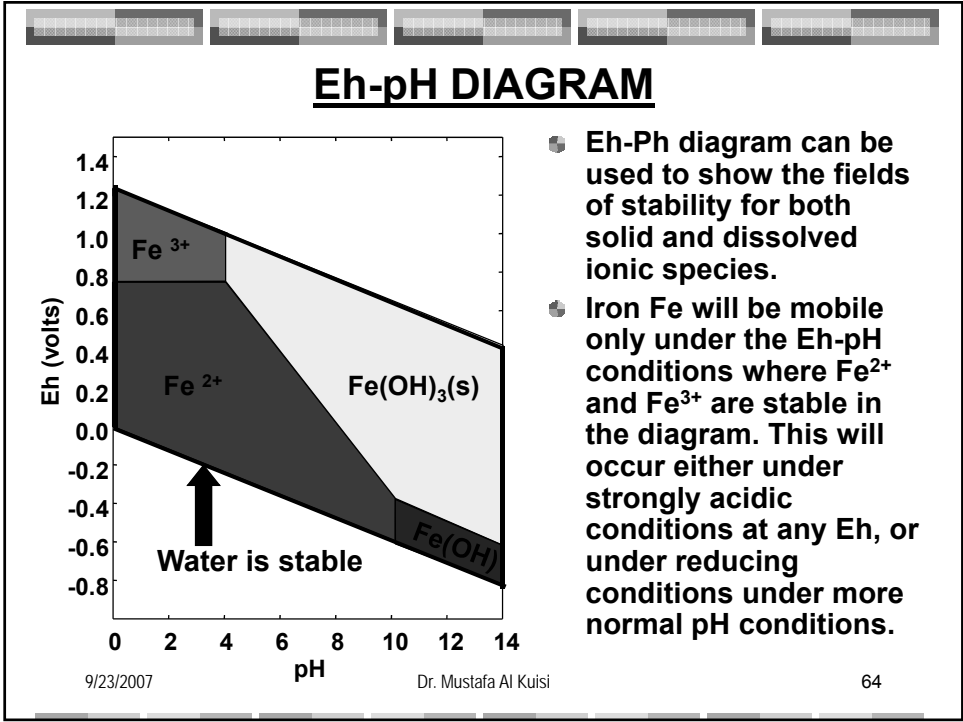
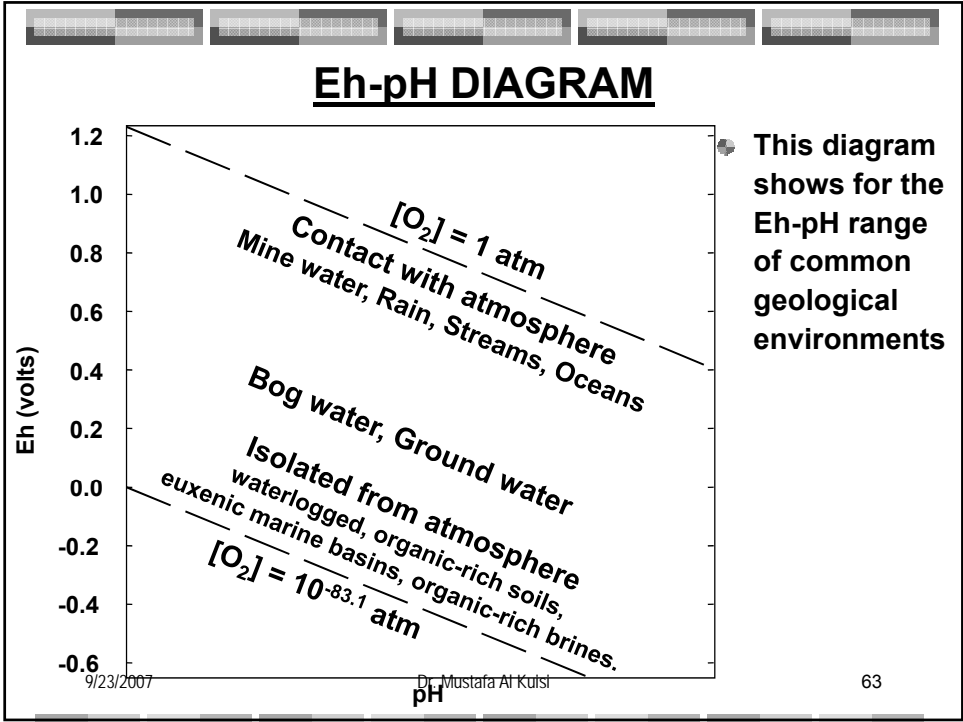
- At conditions above the top dashed line, water is oxidized to O_2 ; at conditions below the bottom dashed line, water is reduced to H_2 . No natural water can persist outside these stability limits for any length of time.

- Water in nature is usually between pH 4 and pH 9.

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CHEMICAL CHARACTERISTICS - 6

- **Dissolved Oxygen (DO) – the only gas routinely measured in water samples (mg/L).**
- **Dissolved oxygen refers to the volume of oxygen that is contained in water. Oxygen enters the water by photosynthesis of aquatic biota and by the transfer of oxygen across the air-water interface. The amount of DO depends on the water temperature, salinity, and pressure.**
- **When performing the dissolved oxygen test, only grab samples should be used, and the analysis should be performed immediately. Therefore, this is a field test that should be performed on site.**
- **As dissolved oxygen levels in water drop below 5.0 mg/L, aquatic life is put under stress. The lower the concentration, the greater the stress.**

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Dissolved Oxygen



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DO – importance and reporting

- Oxygen is produced during photosynthesis and consumed during respiration and decomposition.
- Generally $< 3 \text{ mg/L}$ is stressful to aquatic life.
- Units of measurement are:
 - Concentration: $\text{mg/L} = \text{ppm}$; concentrations range 0.0 to 20 mg/L
 - % saturation – used to determine if water is fully saturated with oxygen at a particular temperature

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DO – techniques

- Probe types and measurement techniques:
 - Winkler titration
 - Amperometric (polarographic) method, most commonly used



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DO – probes

- Most common sensor is the temperature compensated polarographic membrane-type (amperometric)
 - Temperature sensitive (but virtually all are compensated).
 - The probes actually consume O_2 as they work so measurements require moving water using either a built-in stirrer (typical in multiparameter sondes and BOD probes) or “*hand jiggling*” during the measurement.
 - *in situ* sensors are prone to fouling by algal/bacterial slimes and by silt in streams.

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DO probes and meters



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Electrical Conductivity



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EC - importance

- **Cheap, easy way to characterize the total dissolved salt concentration of a water sample**
- **For tracing water masses and defining mixing zones**
 - Groundwater plumes
 - Stream flowing into another stream or into a lake or reservoir

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Principle of measurement

- A small voltage is applied between 2 parallel metal rod shaped electrodes, usually 1 cm apart
- Measured current flow is proportional to the dissolved ion content of the water
- If the sensor is temperature compensated to 25°C, EC is called "*specific*" EC (EC25)

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EC25 - units

- **What in the world are microSiemens per centimeter ($\mu\text{S}/\text{cm}$)?**
- **Units for EC and EC25 are mS/cm or $\mu\text{S}/\text{cm}$ @25°C. The WOW site reports it as EC @25°C (in $\mu\text{S}/\text{cm}$).**
- **Usually report to 2 or 3 significant figures (to $\pm \sim 1\text{-}5 \mu\text{S}/\text{cm}$)**

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EC25

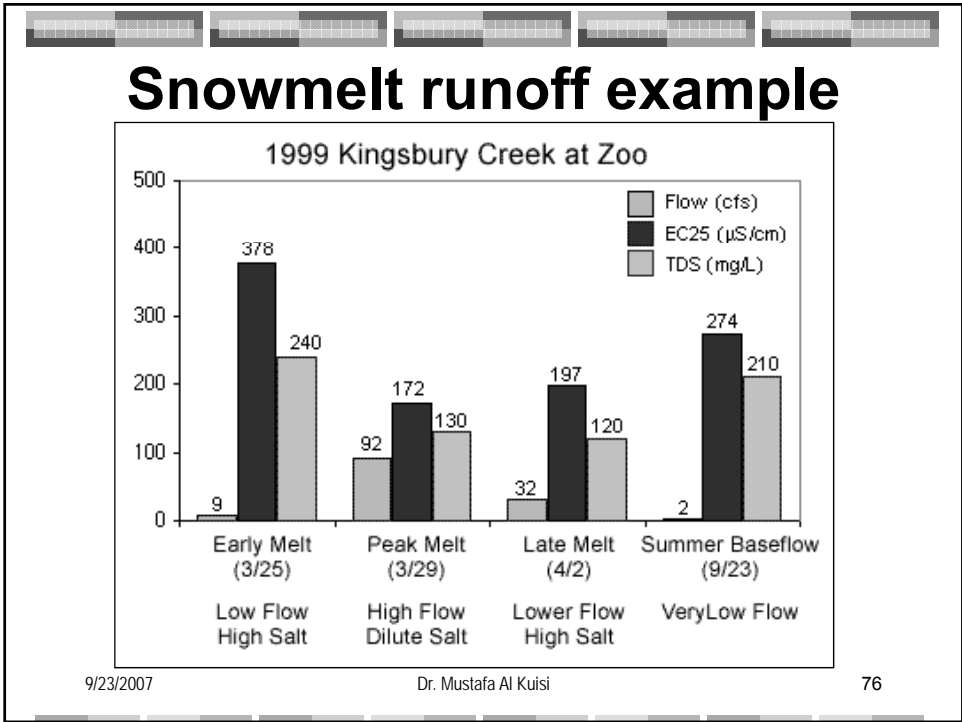
● **EC25 values in streams reflect primarily a combination of watershed sources of salts and the hydrology of the system**

- **wastewater** from sewage treatment plants and industrial discharge
- **wastewater** from on-site wastewater treatment and dispersal systems (septic systems and drainfields)
- **urban runoff**
- **agricultural runoff**
- **acid mine drainage**
- **atmospheric inputs**

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Temperature



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Temperature importance

- Temperature affects:
 - the oxygen content of the water (oxygen levels become lower as temperature increases)
 - the rate of photosynthesis by aquatic plants
 - the metabolic rates of aquatic organisms
 - the sensitivity of organisms to toxic wastes, parasites, and diseases

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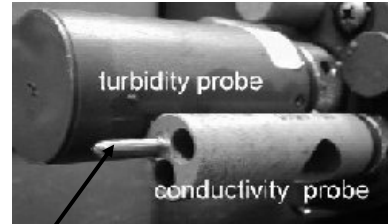
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Temperature measurement - probes

• Types of probes

- Liquid-in-glass
- Thermistor: based on measuring changes in electrical resistance of a semi-conductor with increasing temperature.



thermistor on a YSI sonde

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Temperature changes

• Causes of temperature change include:

- weather
- removal of shading streambank vegetation,
- impoundments (a body of water confined by a barrier, such as a dam)
- discharge of cooling water
- urban storm water
- groundwater inflows to the stream

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Other Water Quality Parameters

- Nutrients – nitrogen and phosphorus
- Fecal coliforms
- Biochemical oxygen demand (BOD)
- Metals
- Toxic contaminants

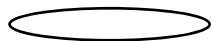
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Fecal coliforms

- Pathogens are number one



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Water sampling - microbes



• Sterile technique:

- Containers must be sterilized by autoclaving or with gas used to kill microbes
- Take care not to contaminate the container
- Water samplers should be swabbed with 70 % alcohol

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Bacteria – *E. coli* and fecal coliforms

- Fecal bacteria are used as indicators of possible sewage contamination
- These bacteria indicate the possible presence of disease-causing bacteria, viruses, and protozoans that also live in human and animal digestive systems
- *E. coli* is currently replacing the fecal coliform assay in most beach monitoring programs

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Water sample collection – grab samples



Grab samples for fecal coliforms are taken with sterile containers

Suggested sample volumes

Analyte	Volume needed
chlorophyll	>500 mLs
TSS	Often > 1 L
total phosphorus total nitrogen anions	200 to 500 mLs
Dissolved nutrients	~ 100mLs
Total and dissolved carbon	~60 mLs
Metals	~60 mLs
color, DOC	~60 mLs

Stream sampling– sample labeling

- An unlabeled sample may as well just be dumped down the drain.
- Use good labels not masking tape, etc. Poor labels often fall off when frozen samples are thawed.
- Use permanent markers **NOT** ball point pens, pencils in a pinch



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Automated stream monitoring



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Water sampling - automated

- Automated stream sampling stations provide continuous monitoring of a variety of parameters
- These units are capable of both collecting water samples and measure various water quality parameters



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Automated stream samplers

- Flow weighted composites
- Flow weighted discrete
- Sampling triggered by predetermined set point such as:
 - Flow
 - Precipitation
 - Any other parameter measured by in-stream sensors

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ALKALINITY

- In aqueous solutions, positive and negative charges must balance.

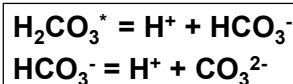
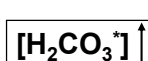
At pH=7, $[H^+] = [OH^-]$

At pH>7, $[H^+] < [OH^-]$ ~ must contain cations other than H^+

- For $CO_2 - H_2O$ system,
possible species are:
the charge-balance equation is:

Note that, each mole of CO_3^{2-} provides two equivalents of negative charge in solution, so the concentration of carbonate must be multiplied by 2.

- If we add more CO_2 into the system,



An equivalent amount of H^+ must also be formed to balance the charge.

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ALKALINITY

- Increasing partial pressure of CO_2
 \Rightarrow Decreasing pH (increased H^+ activity) in solution

♣ What is the partial pressure?

Air is a mixture of many different gases. Each gas in the mixture exerts a pressure called the partial pressure of that gas. Air pressure is the sum of all these partial pressures.

- If we introduce sodium into the system,
the charge-balance equation is:

Then, let's add strong acid. What would be changed?

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ALKALINITY

- For all dissolved species, the charge balance equation can be extended:

$$2[Ca^{+2}] + 2[Mg^{+2}] + [K^+] + [Na^+] + [H^+] + \dots$$

$$= [Cl^-] + 2[SO_4^{-2}] + [NO_3^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + \dots$$
- Let's put all the conservative ions on the left, and all the non-conservative ions on the right.

$$\Sigma \text{ conservative cations} - \Sigma \text{ conservative anions (in equivalents)}$$

$$= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$
- Note that, if the left-hand side of the equation is conservative, then the sum of all the non-conservative species on the right-hand side of the equation must also be conservative. Thus, although none of the individual species on the right is conservative, their mathematical combination as shown is conservative. Therefore, the quantity on the right-hand side of the equation is a special combination, and we call this quantity the ***total alkalinity***.

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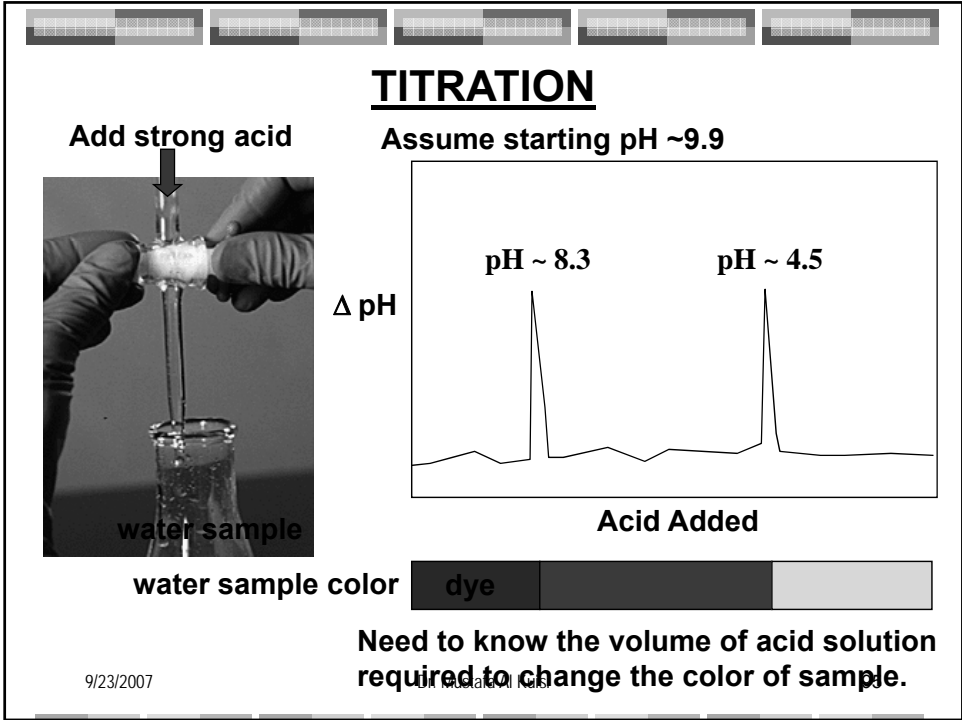
ALKALINITY

- $Alk_T = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$
- Total alkalinity can be changed?
 - add strong acid or base
 - dissolution or precipitation of a solid phase
 - changes in CO_2 partial pressure
- Because precipitation/dissolution reactions can change alkalinity, it is important to measure this quantity immediately in the field.
- Waiting to measure alkalinity in the laboratory is one of the most common reasons for unacceptable charge-balance errors in chemical analyses of natural waters.
- Alkalinity is measured by *titration* with strong acid. A known volume of sample is titrated until an endpoint.

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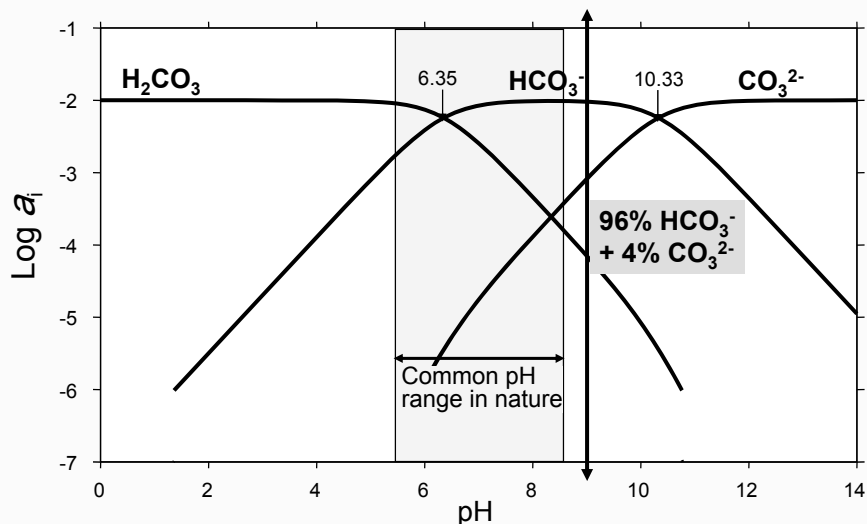
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Bjerrum plot showing the activities of inorganic carbon species as a function of pH for a value of total inorganic carbon of $10^{-3} \text{ mol L}^{-1}$.



In most natural waters, bicarbonate is the dominant carbonate species!

ALKALINITY

- Alkalinity is normally reported by the laboratory in units of mg/L as CaCO_3 (calcium carbonate).

$$\text{Alkalinity (eq/L)} = \text{Alkalinity (mg/L as CaCO}_3) \times 2 \text{ eq/mole}$$

This does not mean that CaCO_3 is necessarily present in the solution. What it means is that the solution has numerically the same alkalinity as a solution in which the same weight of CaCO_3 per liter has been dissolved.

- Calculation of alkalinity from a titration is according to:

$$\text{Alk}_T = \frac{\text{mL}_{\text{acid}} \times N_{\text{acid}} \times \text{eq. wt. CaCO}_3}{\text{mL}_{\text{sample}}}$$

- The equivalent weight of CaCO_3

$$\text{molar mass of CaCO}_3 \frac{100\text{g}}{\text{mole}} \times \frac{1\text{mole}}{2\text{eq}} = 50 \frac{\text{g}}{\text{eq}}$$

recall that an equivalent is essentially a mole of charge

ALKALINITY

Example. A 100 mL sample is titrated to the methyl orange end point with 2 mL of 0.5 N H₂SO₄. What is the total alkalinity in mg L⁻¹ as CaCO₃ and what is the concentration of HCO₃⁻ in mg L⁻¹?

The total alkalinity in mg L⁻¹ as CaCO₃ is given by:

The concentration of HCO₃⁻ is given as:

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WATER HARDNESS

- Hardness - an undesirable property of water resulting from the presence of primarily Ca²⁺ and Mg²⁺ ions.
- Hardness produces a scummy residue and scale on plumbing and sinks.
- Hardness can be expressed as the sum of the calcium and magnesium concentrations, given in equivalents per liter or the equivalent weight of CaCO₃ or ppm as CaCO₃.

Total hardness (eq/L) = Ca²⁺ (eq/L) + Mg²⁺ (eq/L)

Hardness rating	Concentration of CaCO ₃ (mg/L)
Soft	0 to <75
Medium hard	75 to <150
Hard	150 to <300
Very hard	300 and greater

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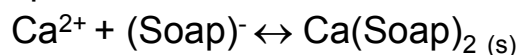
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Hardness

- A term often used to characterize the ability of a water to:

- cause soap scum



- increase the amount of soap needed
- cause scaling on pipes
- cause valves to stick due to the formation of calcium carbonate crystals
- leave stains on plumbing fixtures



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Hardness

● Total Hardness

- Technically - the sum of all polyvalent cations
- Practically - the amount of calcium and magnesium ions (the predominant minerals in natural waters)
- It is divided into carbonate and noncarbonate hardness.

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Hardness

Description	Hardness range (mg/L as CaCO ₃)
Soft	0 - 75
Moderately hard	75 - 100
Hard	100 - 300
Very hard	> 300

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Formation of Hardness

Precipitation

Topsoil

Subsoil

$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$

Limestone

$\text{CaCO}_{3(s)} + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}(\text{HCO}_3)_2$

$\text{MgCO}_{3(s)} + \text{H}_2\text{CO}_3 \rightarrow \text{Mg}(\text{HCO}_3)_2$

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Hardness

• Carbonate Hardness

- Often called "temporary hardness" because heating the water will remove it. When the water is heated, the insoluble carbonates will precipitate and tend to form bottom deposits in water heaters.
- Ca^{2+} , Mg^{2+} associated with HCO_3^- , CO_3^{2-}
- $\text{CH} = \text{TH}$ or Total alkalinity, whichever is less

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Hardness

• Non-Carbonate Hardness

- Called permanent hardness because it is not removed when the water is heated. It is much more expensive to remove non-carbonate hardness than carbonate hardness.
- Ca^{2+} , Mg^{2+} associated with other ions, Cl^- , NO_3^- , SO_4^{2-}
- $\text{NCH} = \text{TH} - \text{CH}$
- If Alkalinity \geq Total hardness, then $\text{NCH} = 0$

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Hardness Units

- milligrams per liter (mg/L) as calcium carbonate
- parts per million (ppm) as calcium carbonate
- grains per gallon of hardness (to convert from grains per gallon to mg/L, multiply by 17.1)
- equivalents/liter
 - equivalents
 - acids and bases: number of H^+ transferred
 - redox reactions: number of e^- transferred

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Hardness Units

- Most common expression of hardness
mg/L of X as $CaCO_3$ =
- Total hardness = $[Ca^{2+}] + [Mg^{2+}] + \dots$
 - can use: M, mM, eq/L, meq/L, mg/L as $CaCO_3$
 - cannot use: mg/L

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Example 6: Calculations

- A sample of water having a pH of 7.2 has the following concentrations of ions
 - Ca²⁺ 40 mg/L
 - Mg²⁺ 10 mg/L
 - Na⁺ 11.8 mg/L
 - K⁺ 7.0 mg/L
 - HCO₃⁻ 110 mg/L
 - SO₄²⁻ 67.2 mg/L
 - Cl⁻ 11 mg/L
- Calculate the TH, CH, NCH, Alkalinity

Example 6: Calculations

Ion	Conc. mg/L	M.W. mg/mmol	n	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as CaCO ₃
Ca ²⁺	40.0	40.1				
Mg ²⁺	10.0	24.3				
Na ⁺	11.8	23.0				
K ⁺	7.0	39.1				
HCO ₃ ⁻	110.0	61.0				
SO ₄ ²⁻	67.2	96.1				
Cl ⁻	11.0	35.5				

Example 6: Calculations

Ion	Conc. mg/L	M.W. mg/mmol	_n	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as CaCO ₃
Ca ²⁺	40.0	40.1	2	20.05		
Mg ²⁺	10.0	24.3	2	12.15		
Na ⁺	11.8	23.0	1	23.0		
K ⁺	7.0	39.1	1	39.1		
HCO ₃ ⁻	110.0	61.0	1	61.0		
SO ₄ ²⁻	67.2	96.1	2	48.05		
Cl ⁻	11.0	35.5	1	35.5		

Sample Calculation: Equivalent Weight of Ca²⁺ = M.W. / |_n|
= 40.1/2 = 20.05

Example 6: Calculations

Ion	Conc. mg/L	M.W. mg/mmol	_n	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as CaCO ₃
Ca ²⁺	40.0	40.1	2	20.05	1.995	
Mg ²⁺	10.0	24.3	2	12.15	0.823	
Na ⁺	11.8	23.0	1	23.0	0.51	
K ⁺	7.0	39.1	1	39.1	0.179	
HCO ₃ ⁻	110.0	61.0	1	61.0	1.80	
SO ₄ ²⁻	67.2	96.1	2	48.05	1.40	
Cl ⁻	11.0	35.5	1	35.5	0.031	

Sample Calculation: Concentration of Ca²⁺ =
(Concentration in mg/L) / (Equivalent Weight in mg/meq) =
(40.0 mg/L) / (20.05 mg/meq) = 1.995 meq/L

Ion	Conc. mg/L	M.W. mg/mmol	n	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as CaCO ₃
Ca ²⁺	40.0	40.1	2	20.05	1.995	99.8
Mg ²⁺	10.0	24.3	2	12.15	.823	41.2
Na ⁺	11.8	23.0	1	23.0	.51	25.7
K ⁺	7.0	39.1	1	39.1	.179	8.95
HCO ₃ ⁻	110.0	61.0	1	61.0	1.80	90.2
SO ₄ ²⁻	67.2	96.1	2	48.05	1.40	69.9
Cl ⁻	11.0	35.5	1	35.5	.031	15.5

Sample Calculation: Concentration of Ca²⁺ in mg/L as CaCO₃ =
(Concentration in meq/L) * (Equivalent Weight of CaCO₃) =
(1.995 meq/L) / (50 mg/meq) = 99.8 mg/L as CaCO₃

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Example 6: Calculations

- Check Solution**

$$\begin{array}{rcl} \Sigma(\text{cations}) & = & \Sigma(\text{anions}) \quad \text{to within } \pm 10\% \\ 175.6 & = & 175.6 \quad \text{mg/L as CaCO}_3 \end{array}$$

(Can check using concentrations in meq/L or mg/L as CaCO₃)
- Total Hardness = Σ of multivalent cations**

$$\begin{aligned} &= (\text{Ca}^{2+}) + (\text{Mg}^{2+}) = 99.8 + 41.2 = \\ &141 \text{ mg/L as CaCO}_3 \end{aligned}$$

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Example 6: Calculations

- **Carbonate Hardness** (the portion of the hardness associated with carbonate or bicarbonate)
 - Alkalinity = 90.1 mg/L as CaCO_3
 - TH = 141 mg/L as CaCO_3
 - CH = 90.1 mg/L as CaCO_3
 - (Note: if TH < Alk then CH = Alkalinity; and NCH = 0)
- **Non-carbonate Hardness**
 - NCH = TH - CH = 141 - 90.1 =
50.9 mg/L as CaCO_3

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CHEMICAL CHARACTERISTICS - 5

- **TDS (Total Dissolved Solids) - TDS meter**

This meter works by measuring the *electrical conductivity* of the water. Conductivity increases as the amounts of salts and other dissolved solids increase in the water. Conductivity and TDS are two different but related tests. One can be calculated from the other by multiplying or dividing by a certain fixed number.

TDS (mg/L) = 0.55 to 0.7 x conductivity of sample ($\mu\text{S/cm}$)

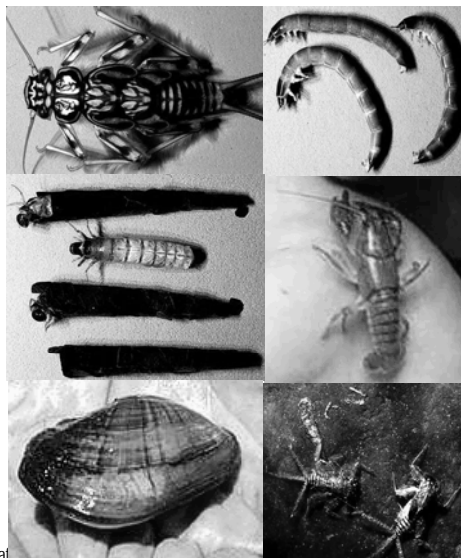
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BIOLOGICAL ASSESSMENT

- Benthic macroinvertebrates are examined to assess the biological attributes of water quality.
- These organisms are abundant, easier to capture than fish, and easier to identify than algae or protozoa.
- Their presence indicates a high quality of water, while their absence suggests water may be polluted.



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CHEMICAL ASSESSMENT

- Commonly measured chemical parameters are:
 - pH
 - Alkalinity
 - Hardness
 - Nitrates, Nitrites, & Ammonia
 - Phosphates
 - Dissolved Oxygen & Biochemical Oxygen Demand
 - Fecal Coliform (bacteria) – too small to detect during the biological assessment.
 - Conductivity

Portable laboratories
and test kits



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pH

- Whether a water will be scale-forming or corrosive?
- Langelier Saturation Index (LI)
 - Determines if calcium carbonate is going to precipitate
 - $LSI = pH - pH_s$
 - pH = actual pH value measured in the water
 - pH_s = pH of the water in equilibrium with solid $CaCO_3$
 - If $LSI > 0$ calcium carbonate will precipitate
 - If $LSI < 0$ calcium carbonate won't precipitate
 - The $CaCO_3$ layer deposited on pipe surfaces acts as a protective coating.
- Ryznar Index
 - Determines the degree of scale formation
 - $RI = 2 pH_s - pH$
 - If $RI < 5.5$ heavy scale will form
 - If $5.5 < RI < 6.2$ scale will form
 - If $6.2 < RI < 8.5$ water is corrosive
 - If $RI > 8.5$ water is very corrosive

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- pH of the water in equilibrium with solid $CaCO_3$

$$pH_s = -\log \left(\frac{K_2 \gamma_{Ca^{+2}} [Ca^{+2}] \gamma_{HCO_3^-} [HCO_3^-]}{K_{SP}} \right)$$

$$\text{where } K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \text{equilibrium constant}$$

γ_i = activity coefficient

K_{SP} = solubility product

- Estimating the activity coefficient γ_i

- Debye-Hückel method

: accurate up to $I \sim 0.01$ M

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

where A = a constant depending on P & T

z_i = the charge on the particular ion

I = the ionic strength

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● **Estimating the activity coefficient γ_i – continued**

- **Davies method (usually adequate for fresh water)**
: accurate up to $I \sim 0.1$ M

$$\log \gamma_i = -Az^2 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2I \right)$$

- **Güntelberg method : accurate up to $I \sim 0.1$ M**

$$\log \gamma_i = -\frac{0.5(z_i)^2 I^{1/2}}{1 + I^{1/2}}$$

● **Estimating the ionic strength I in solution**

$$I = \frac{1}{2} \sum m_i z_i^2$$

where m = molar concentration

$$I = (2.5 \times 10^{-5}) \times \text{TDS (mg/L)} \quad \text{by Langelier}$$

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Example. Determine the Langelier & Ryznar indexes for the Denver water supply. The characteristics of the water are summarized.

Constituent	Conc. (mg/L)	Conc. (mol/L)
TDS	179	-
Ca^{+2}	42	1.05×10^{-3}
HCO_3^-	115	1.89×10^{-3}
pH = 7.9, Temp = 20°C		

- **Determine the ionic strength in solution based on TDS.**
- **Determine activity coefficients for HCO_3^- using Güntelberg method .**
- **Determine activity coefficients for Ca^{+2} using Güntelberg method .**
- **Determine the value of pH_s .**
- **Determine the Langelier index.**
- **Determine the Ryznar index.**

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♣ Carbonate Equilibrium Constants as a Function of Temperature

T, °C	K _m	K ₁ , mol/L	K ₂ , mol/L	K _{sp} , mol ² /L ²
5		3.02 x 10 ⁻⁷	2.75 x 10 ⁻¹¹	8.13 x 10 ⁻⁹
10		3.46 x 10 ⁻⁷	3.24 x 10 ⁻¹¹	7.08 x 10 ⁻⁹
15		3.80 x 10 ⁻⁷	3.72 x 10 ⁻¹¹	6.03 x 10 ⁻⁹
20		4.17 x 10 ⁻⁷	4.17 x 10 ⁻¹¹	5.25 x 10 ⁻⁹
25	1.58 x 10 ⁻³	4.47 x 10 ⁻⁷	4.68 x 10 ⁻¹¹	4.57 x 10 ⁻⁹
40		5.07 x 10 ⁻⁷	6.03 x 10 ⁻¹¹	3.09 x 10 ⁻⁹
60		5.07 x 10 ⁻⁷	7.24 x 10 ⁻¹¹	1.82 x 10 ⁻⁹

$$K_m = \frac{[H_2CO_3]}{[CO_2]_{aq}}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

K_{sp} = Solubility product constant for CaCO₃

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NITROGEN (N)

- Nitrogen gas (N₂) makes up 78.1% of the Earth's air.
- Nitrogen is an essential *nutrient* that is required by all plants and animals for the formation of amino acids (the molecular units that make up protein).
- In order for N to be used for growth it must be "fixed" (combined) in the form of ammonia (NH₃) or nitrate (NO₃).
 - N₂ + 8H⁺ + bacteria = 2NH₃ + H₂
 - NH₃ + O₂ + bacteria = NO₂⁻ + 3H⁺ + 2e⁻
 - NO₂⁻ + H₂O + bacteria = NO₃⁻ + 2H⁺ + 2e⁻
- Ammonia (NH₃) continually changes to ammonium (NH₄⁺) and vice versa, with the relative concentrations of each depending on the water's temperature and pH. Ammonia is extremely toxic; ammonium is relatively harmless. At higher temperatures and pH, more of the nitrogen is in the toxic ammonia form than at lower pH.

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NITROGEN (N)

- **Maximum Contaminant Level (MCL)**
 - nitrite-N : 1 mg/L
 - nitrate-N : 10 mg/L
 - nitrite + nitrate (as N) : 10 mg/L
- **Sources of Contaminant in Drinking Water**
Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
- **Potential Health Effects from Ingestion of Water**
Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.
- **Excessive concentrations of nitrogen can lead to eutrophication and subsequent degradation of stream water quality.**

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PHOSPHATES

- Phosphorus is an essential *nutrient* for for all life forms.
- Never found free in nature, it is widely distributed in combination with minerals.
- Phosphorus is usually present in natural water as phosphates (PO_4^{-3} ; orthophosphates, polyphosphates, and organically bound phosphates)
- **Factors Affecting Phosphorus Concentrations**
 - Wastewater and Septic System Effluent - Organic phosphates are contributed to sewage by body waste and food residues.
 - Detergents
 - Fertilizers
 - Animal Waste
 - Development/Paved Surfaces - Development can cause soil erosion, which will release phosphorus.
 - Industrial Discharge - Phosphates are often added to water to prevent iron oxides or calcium carbonates from forming.
 - Forest Fires – can cause soil erosion

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PHOSPHATES

- No national or state criteria have been established for concentrations of phosphorus compounds in water.
- EPA recommendations
 - total phosphate should not exceed 0.05 mg/L (as phosphorus) in a stream at a point where it enters a lake or reservoir
 - total phosphate should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs
- Excessive concentrations of phosphate can lead to eutrophication and subsequent degradation of stream water quality.
- Up to 4 grams per day does not appear to have any negative side effects. Higher levels cause gastrointestinal discomfort and bone density problems.

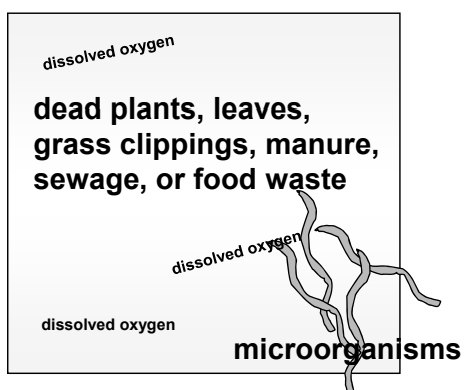
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BIOCHEMICAL OXYGEN DEMAND (BOD)

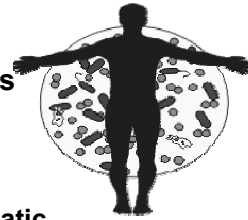
- Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose this waste.
- Nitrates and phosphates are plant nutrients and can contribute to high BOD levels.
- When BOD levels are high, dissolved oxygen (DO) levels decrease \Rightarrow fish and other aquatic organisms may not survive - index of the degree of organic pollution in water
- BOD level of 1-2 ppm - very good
- BOD level of 3-5 ppm - moderately clean
- BOD level of 6-9 ppm - somewhat polluted



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FECAL COLIFORM

- **Harmless bacteria ~ present in large numbers in the feces and intestinal tracts of humans and other warm-blooded animals**
- **Environmental Impact:**
 - The presence of fecal coliform bacteria in aquatic environments indicates that the water has been contaminated with the fecal material of man or other animals.
 - At the time this occurred, the source water may have been contaminated by pathogens or disease producing bacteria or viruses which can also exist in fecal material.
- **Methodology:** Membrane filtration
- **Criteria**
 - Swimming ~ fewer than 200 colonies/100 mL
 - Fishing and boating ~ fewer than 1000 colonies/100 mL
 - Domestic water supply ~ fewer than 2000 colonies/100 mL.
 - There cannot be any fecal coliforms in drinking water.



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CONDUCTIVITY

- **The ability of water to carry an electrical current**
- **An indirect measure of the presence of dissolved solids**
- **Factors affecting conductivity**
 - Geology and soil in the watershed
 - Acid mine drainage
 - Agricultural runoff
 - Road runoff
- **Generally, there aren't regulatory levels for conductivity. Instead, the concentration of total dissolved solids (TDS) is often regulated.**
- **TDS 500 mg/L in drinking water - secondary drinking water standards by EPA**

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PHYSICAL ASSESSMENT

- **Turbidity (a measure of water clarity) cannot go above 5 nephelometric turbidity units (NTUs) by EPA.**
- **Total Suspended Solids (TSS) – High TSS causes less dissolved oxygen to be released into the water by plants.**
- **Total Dissolved Solids (TDS) is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and/or high water hardness, and could result in a laxative effect.**

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Water Quality Information References

- **Colorado Department of Public Health and Environment - Water Quality Control Division**
 - <http://www.cdphe.state.co.us/wq/wqhom.asp>
- **U.S. EPA - National Primary Drinking Water Regulations**
 - <http://www.epa.gov/safewater/mcl.html>
- **U.S. Geological Survey - National Water Quality Assessment Program**
 - <http://water.usgs.gov/nawqa/circ-1136.html>
- **U.S. Department of Agriculture - National Extension Water Quality Database**
 - <http://hermes.ecn.purdue.edu/server/water>

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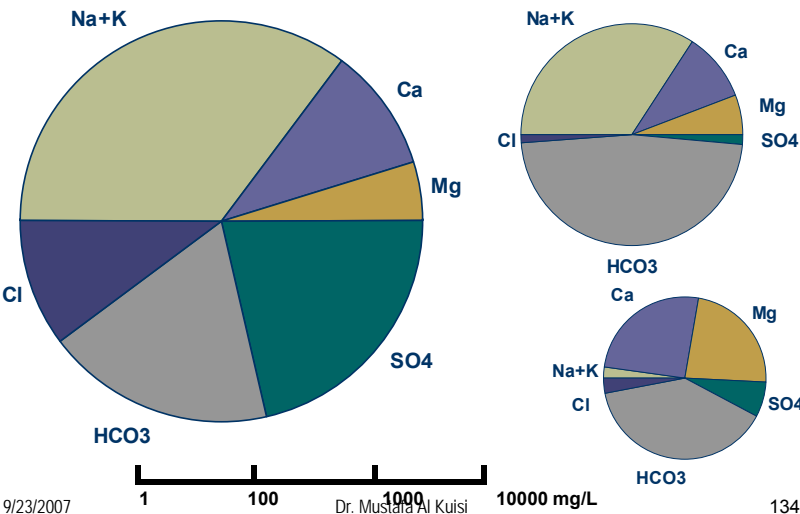
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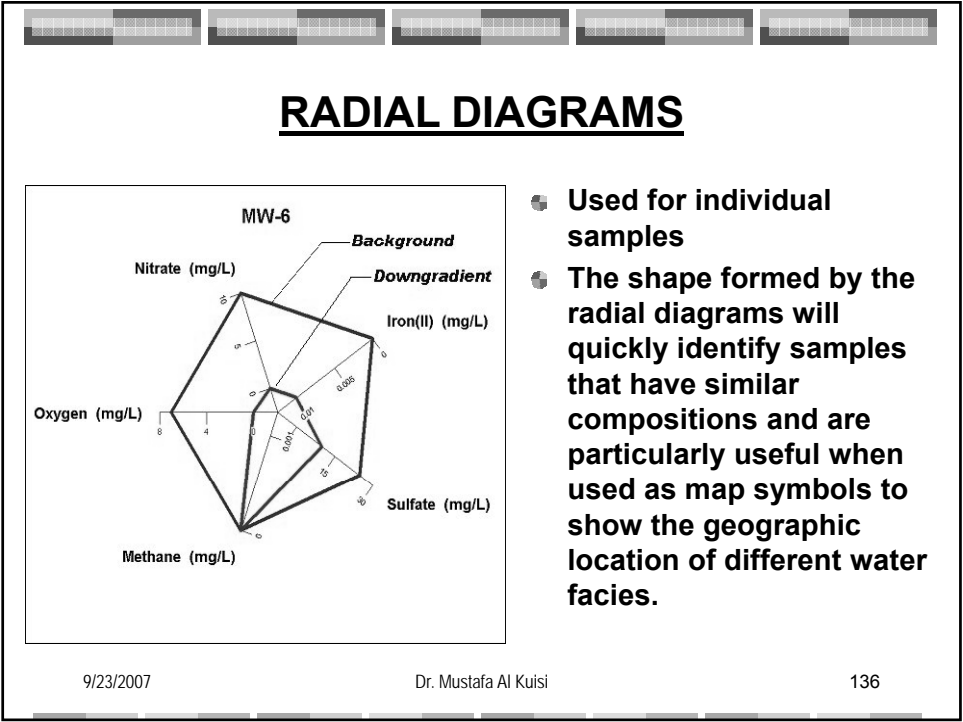
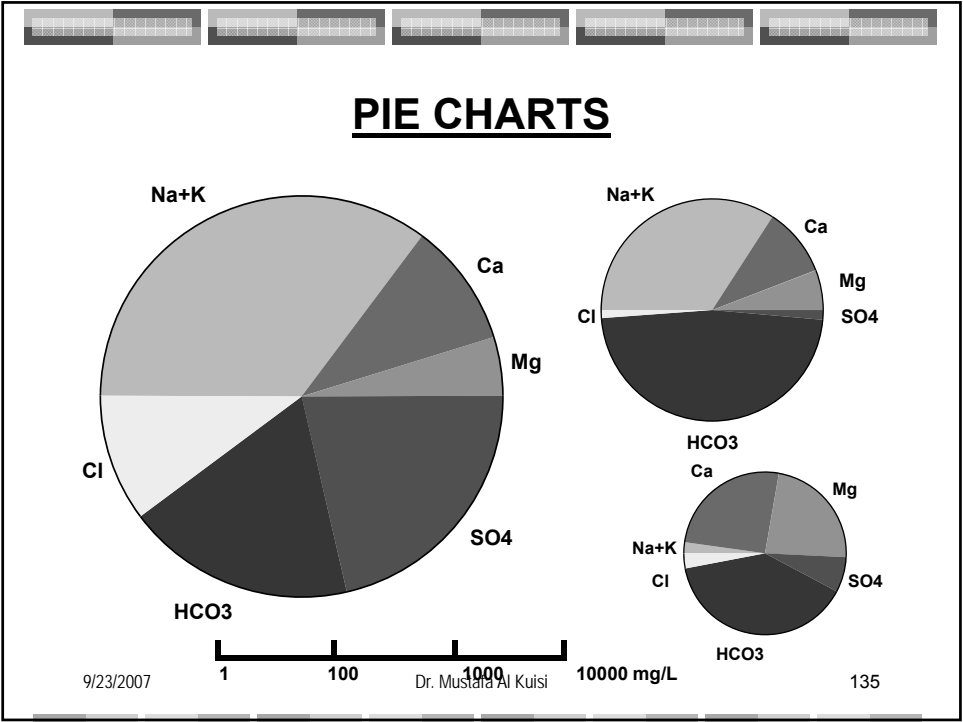
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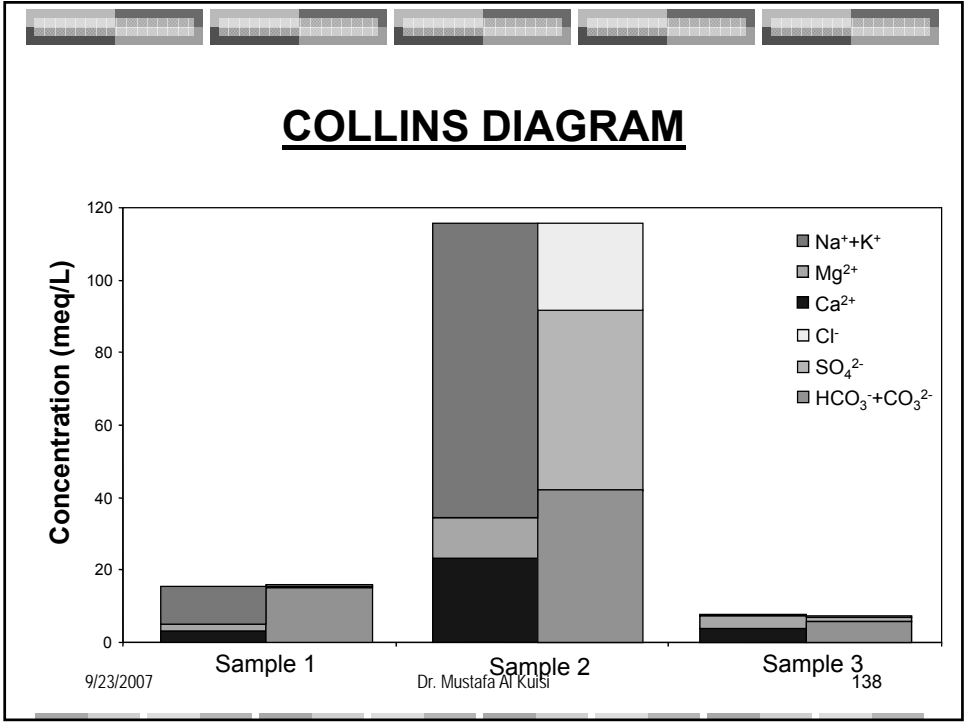
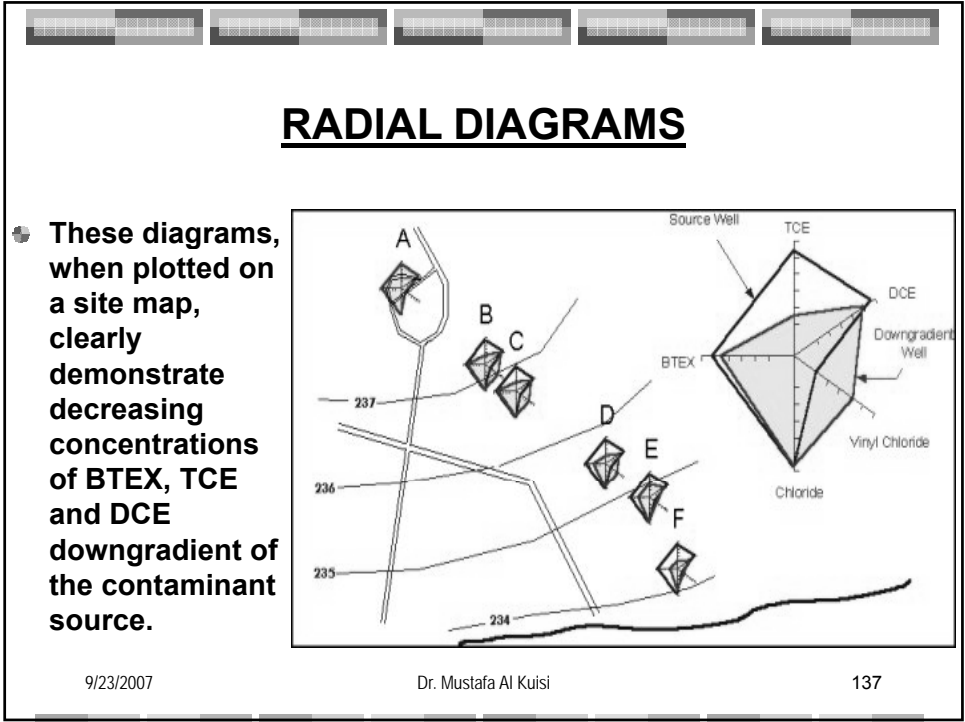
Visualizing Chemical Data

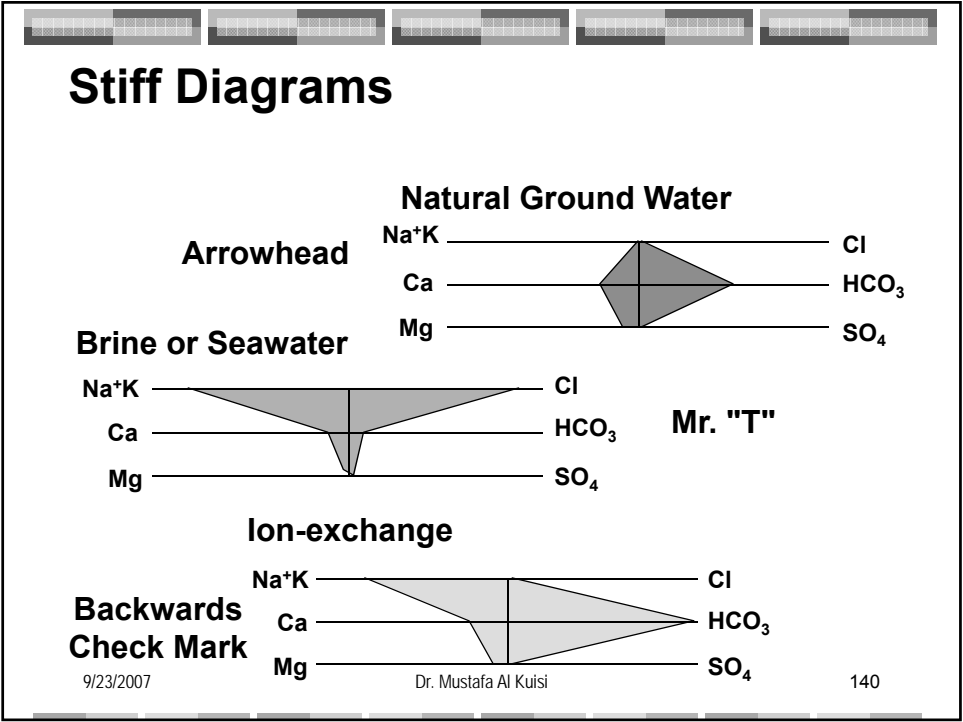
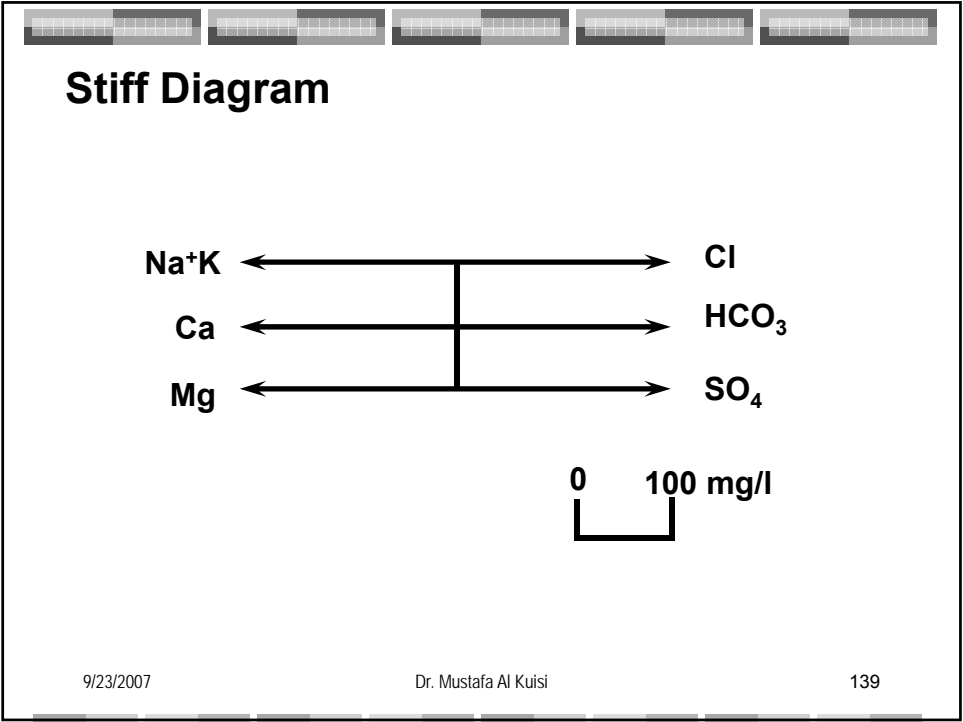
- There are a large number of plots used to visualize ion abundances:
 - Pie Chart
 - Collins Diagram (Bar Chart)
 - Stiff Diagram
 - Shooler Diagram
- Other plots are use to group waters and interpret their origins:
 - Piper Diagram

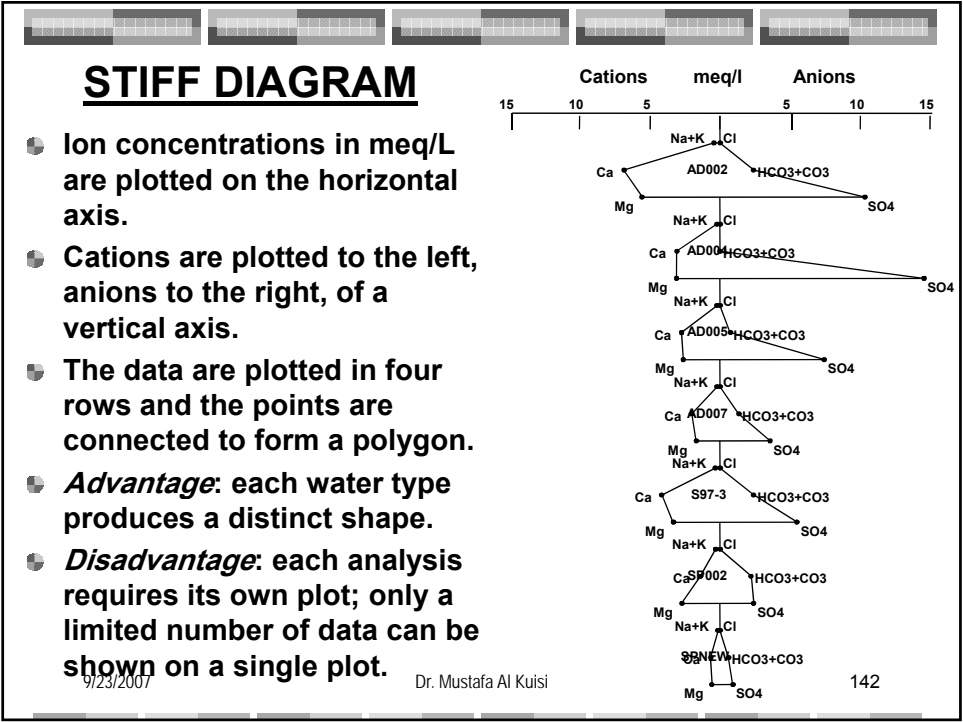
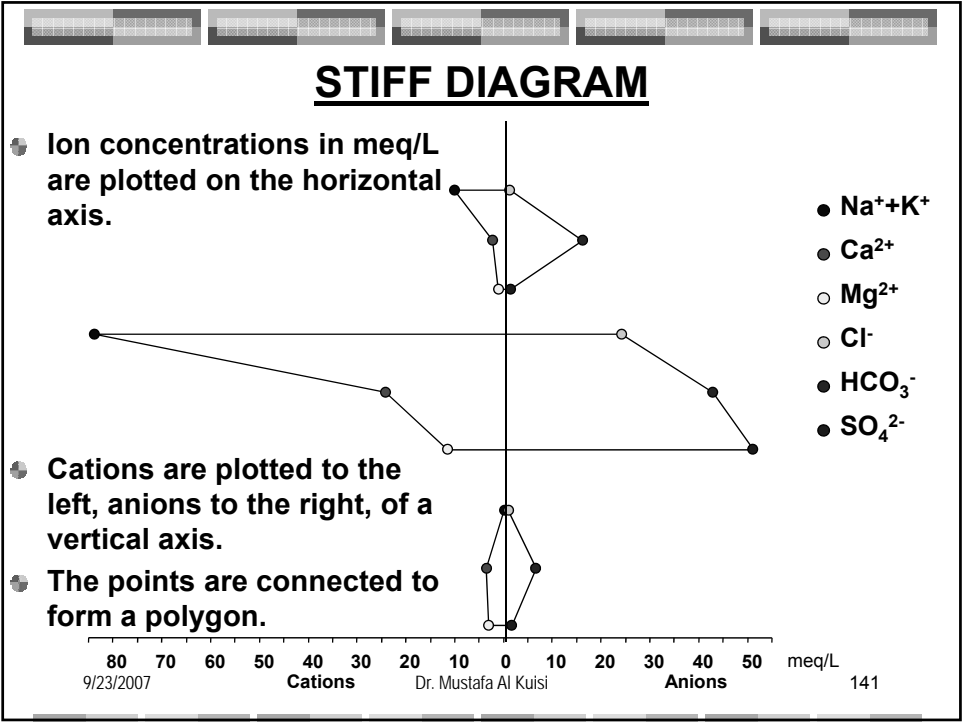
Pie Charts

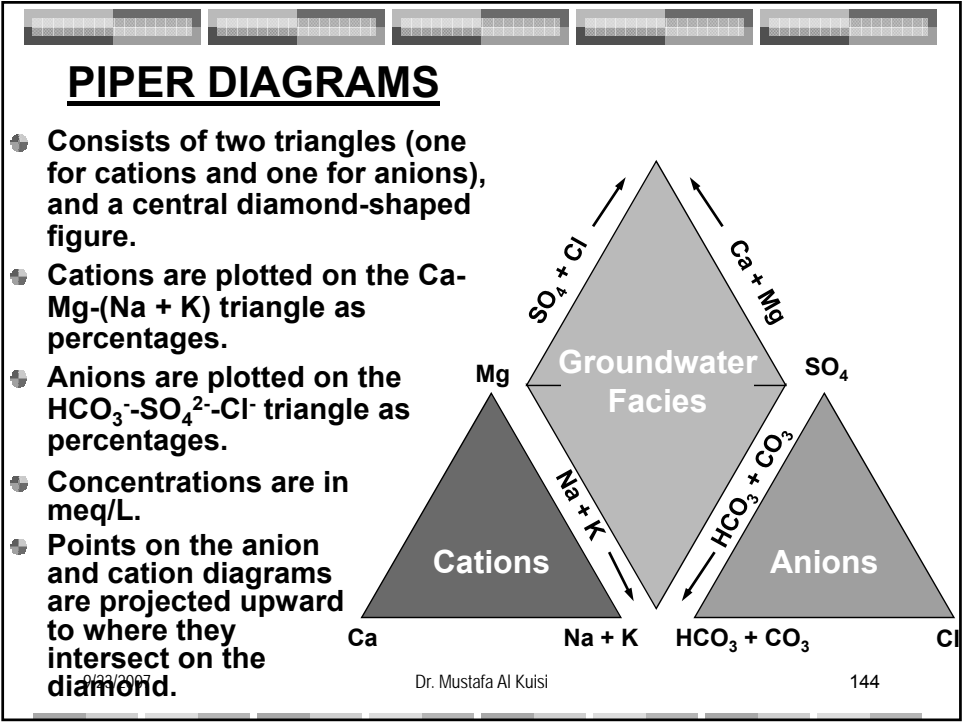
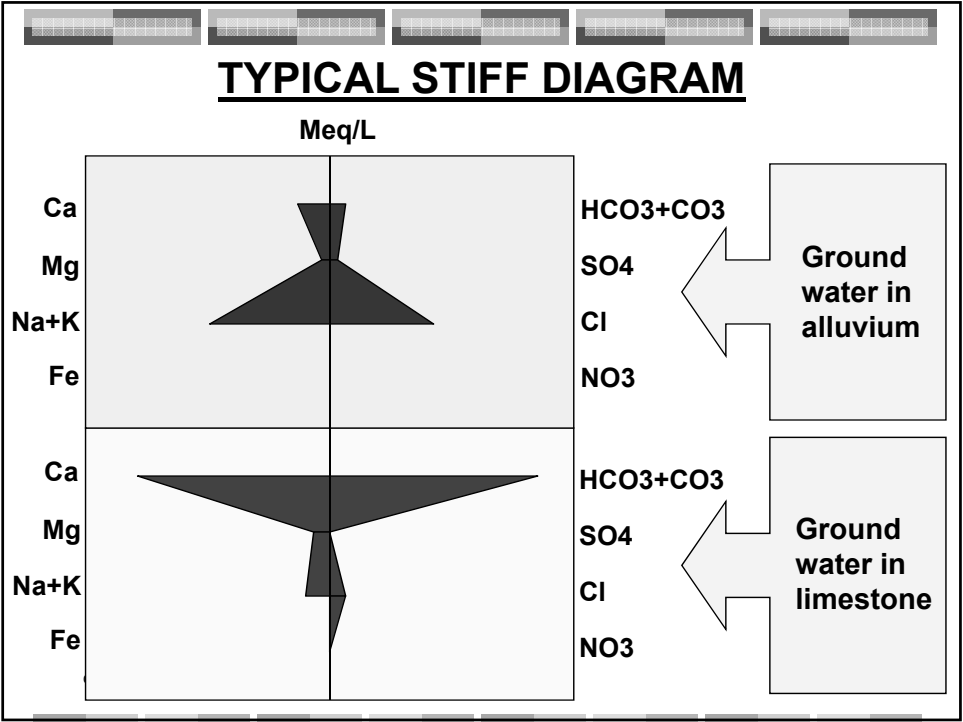












PIPER DIAGRAMS

ADVANTAGES

- Many water analyses can be plotted on the same diagram.
- Can be used to classify waters.
- Can be used to identify mixing of waters.

DISADVANTAGE

- Concentrations are renormalized. Cannot easily accommodate waters where other cations or anions may be significant.

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Piper Diagrams

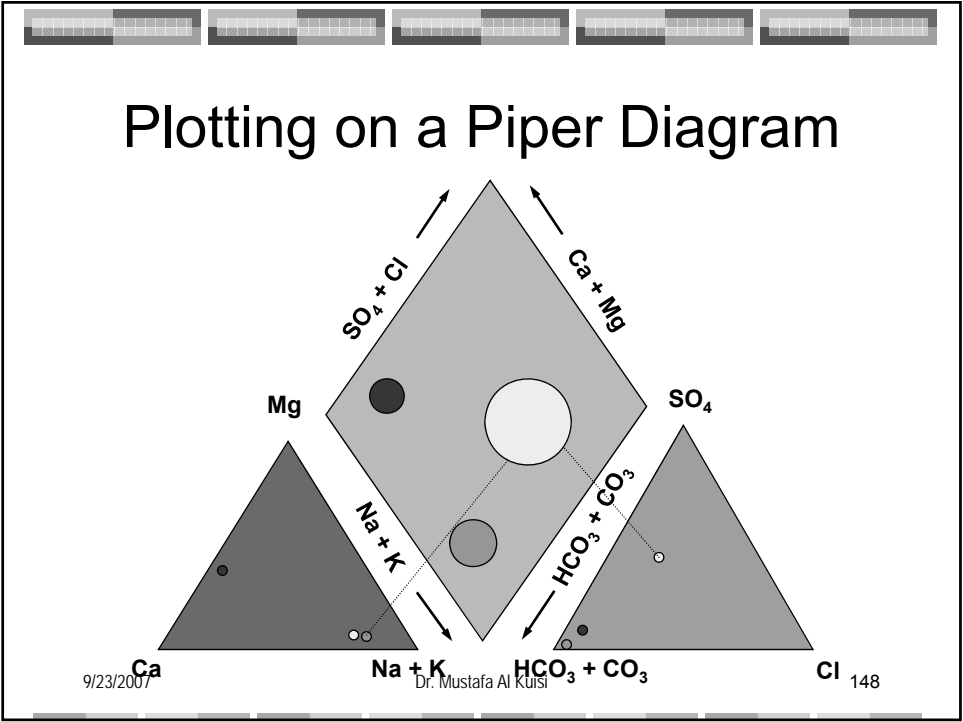
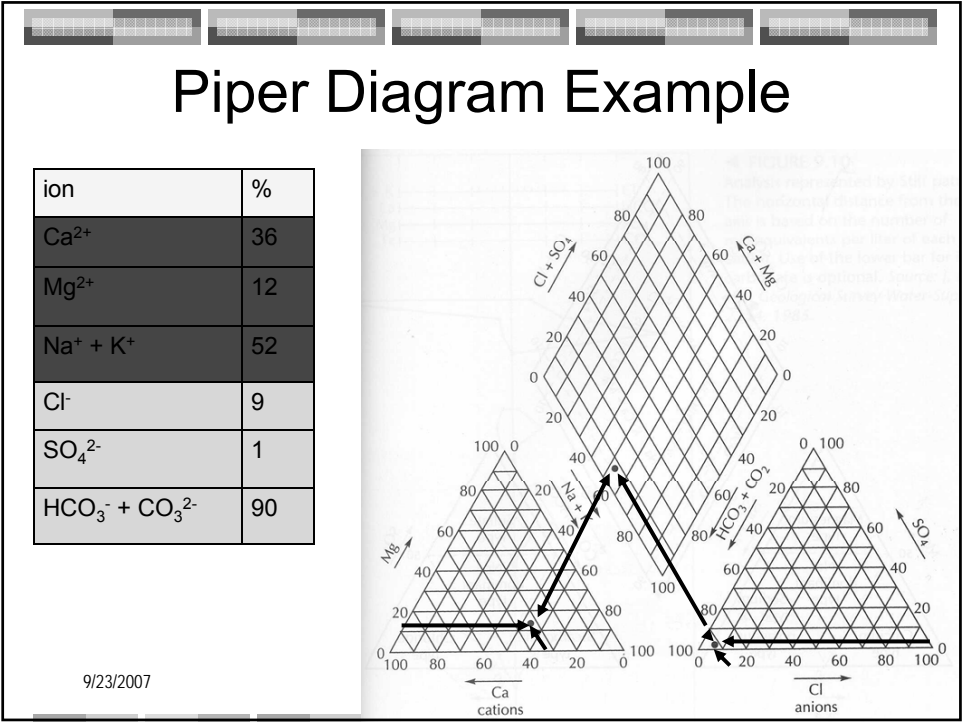
Given the following water analyses, present them on a Piper Diagram.

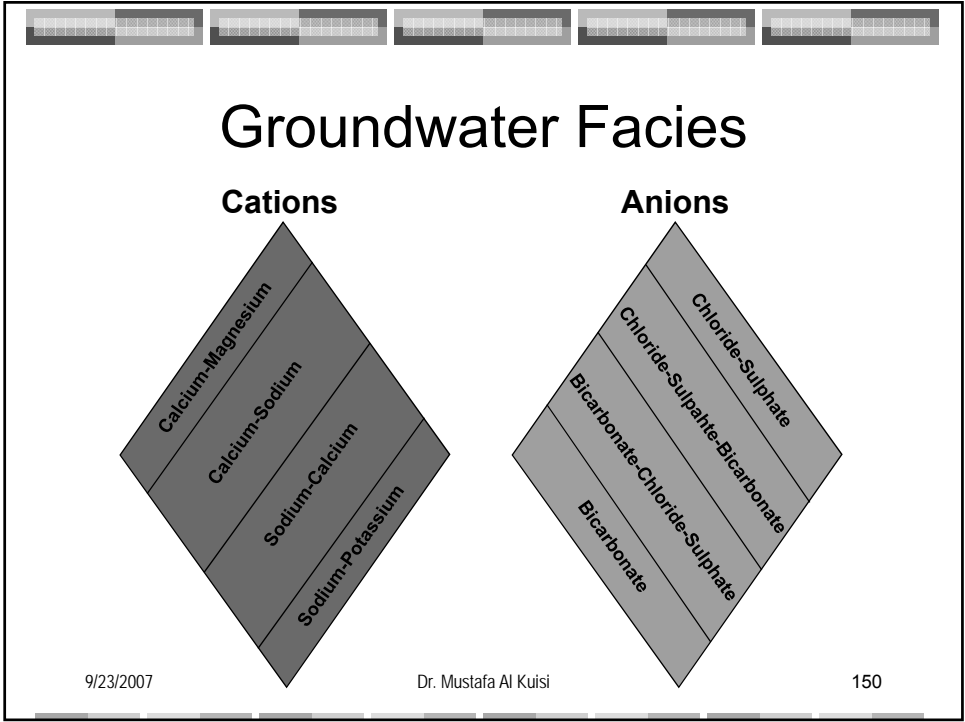
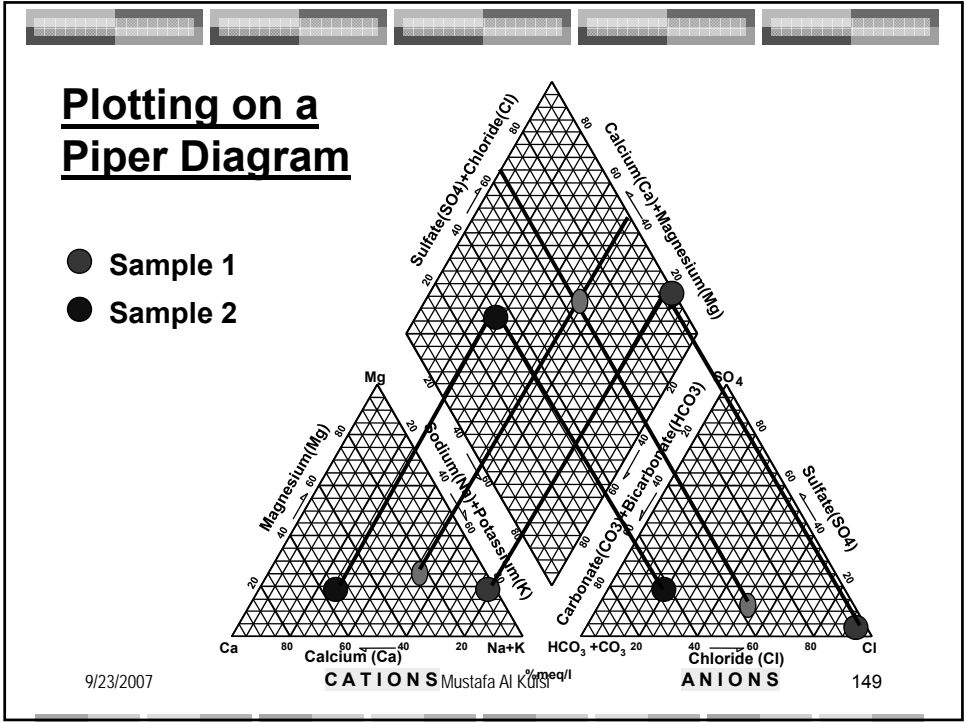
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻
mg/L	23	4.7	35	4.7	171	0	1	9.5
meq/L	1.15	0.39	1.52	0.12	2.8	0	0.02	0.27

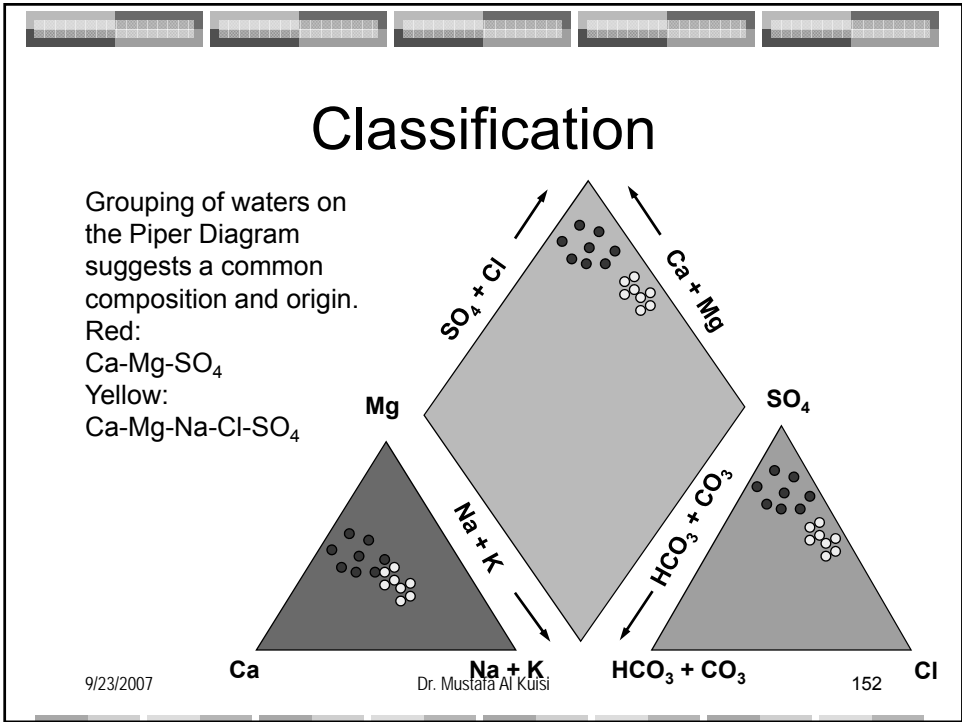
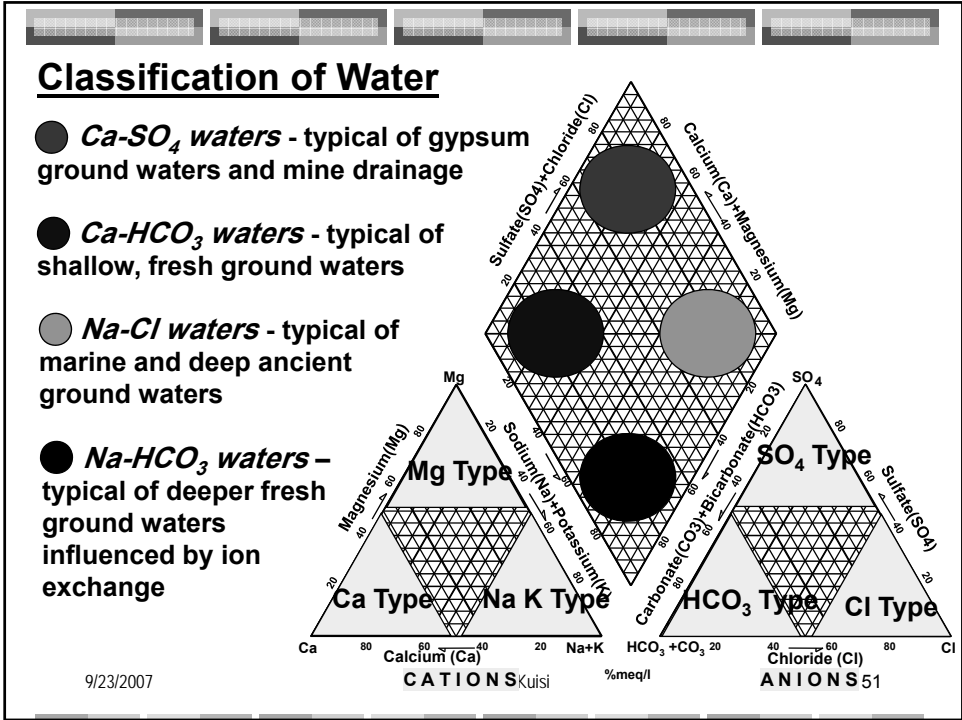
The first step is to find the percent of each cation and anion group as a percentage of the total.

Cations	meq/L	% of total	Anions	meq/L	% of total
Ca ²⁺	1.15	36	Cl ⁻	0.27	9
Mg ²⁺	0.39	12	SO ₄ ²⁻	0.02	1
Na ⁺ + K ⁺	1.64	52	CO ₃ ²⁻ + HCO ₃ ⁻	2.80	90
Total	3.18		Total	3.09	

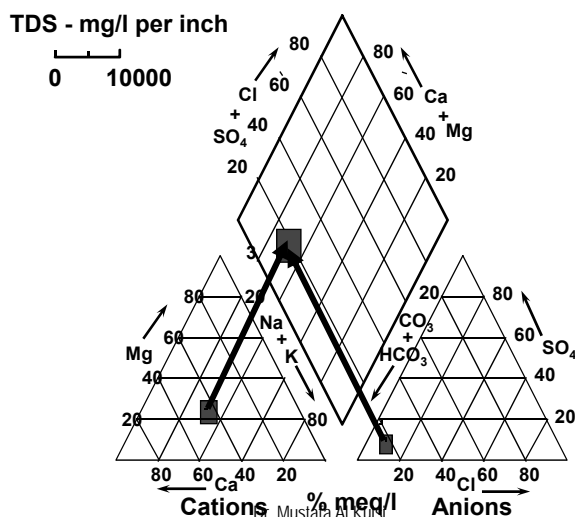
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Piper Diagrams



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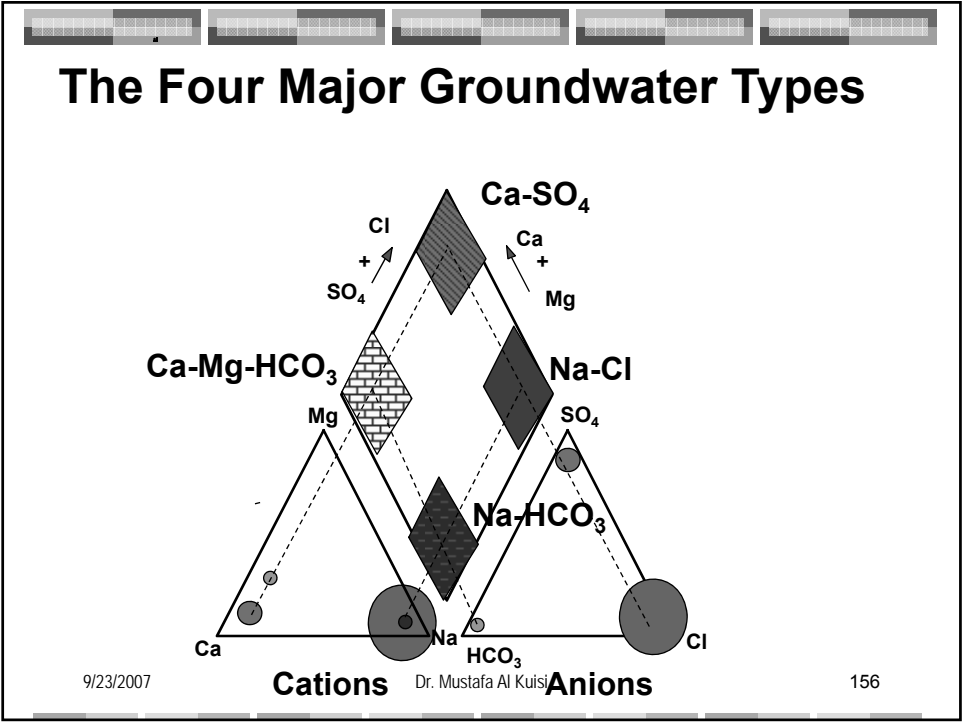
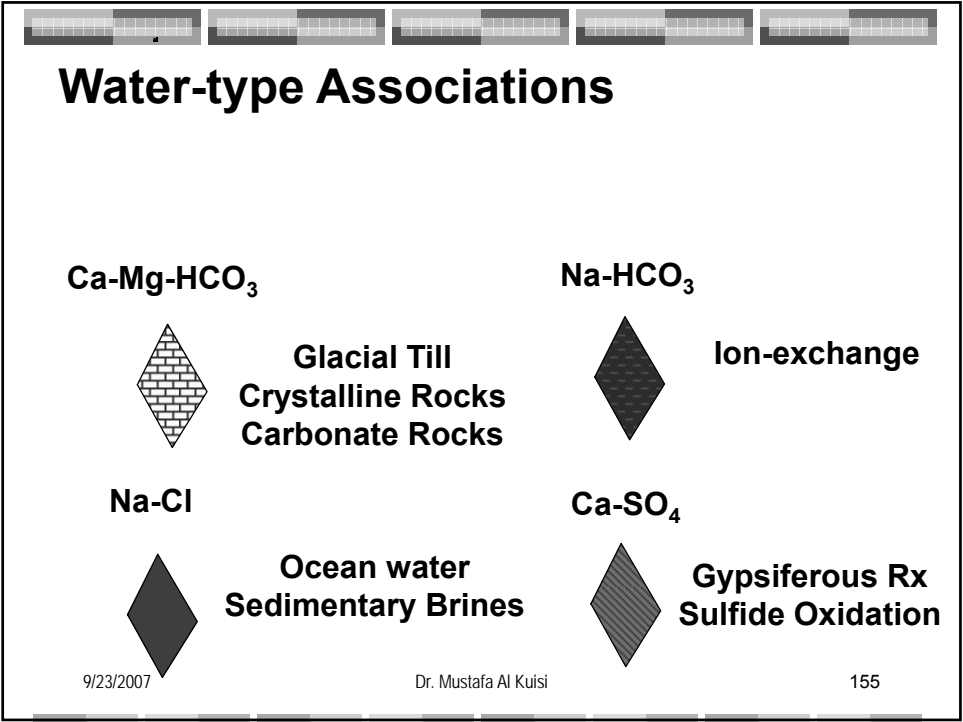
To Prepare a Piper Plot:

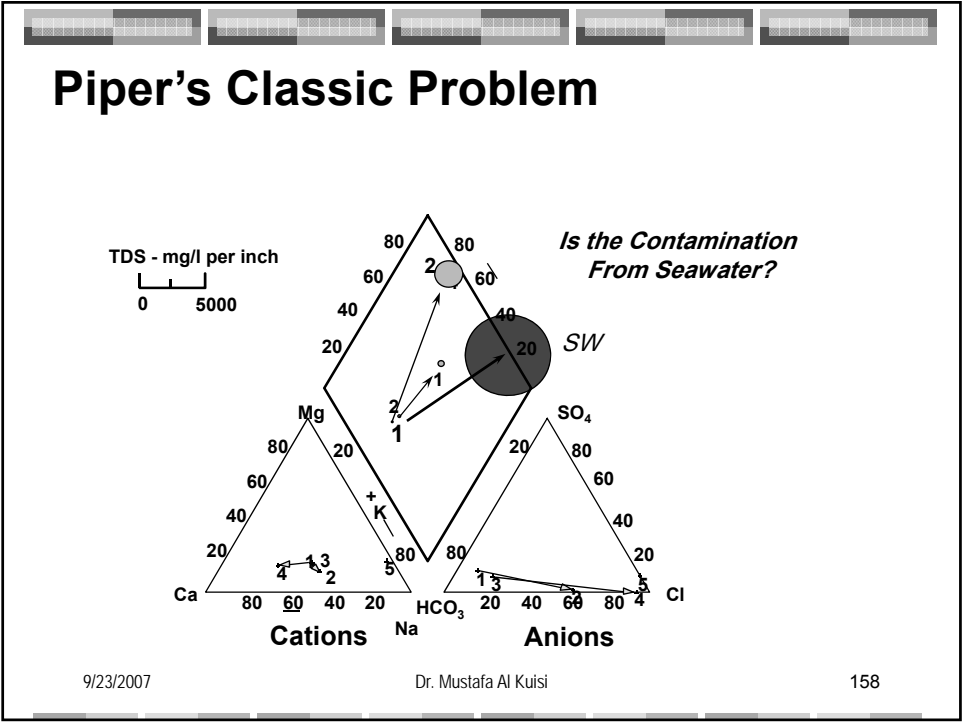
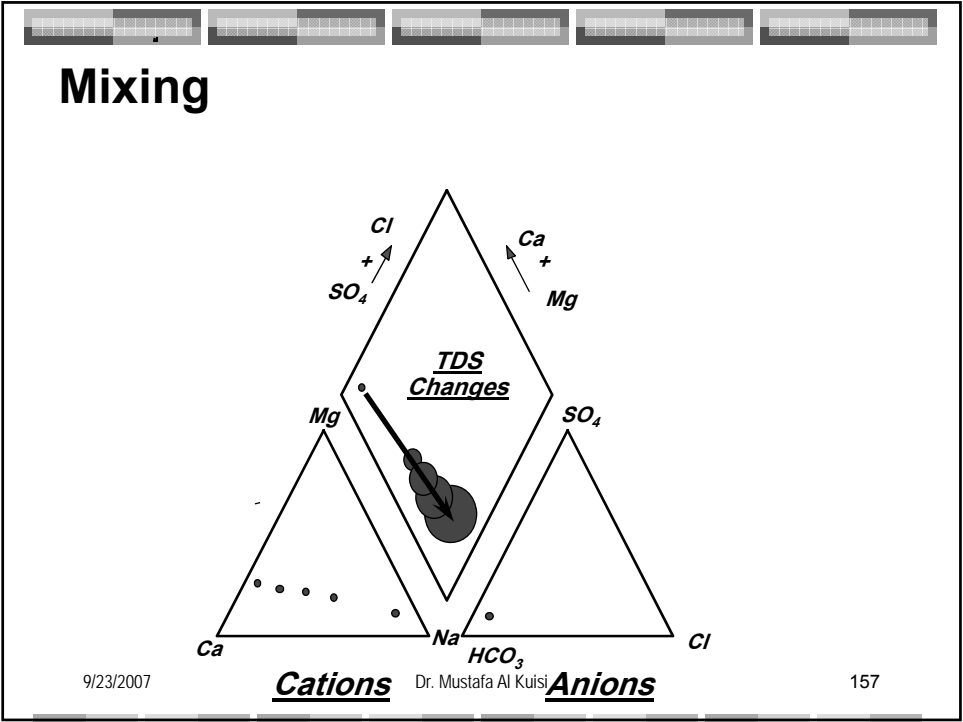
1. Convert mg/L to meq/L.
2. Add cation meq/L together.
Add anion meq/L together.
3. Divide each cation meq/L by total cation meq/L.
Divide each anion meq/L by total anion meq/L.
4. Multiply results of step 3 by 100 to get % meq/L.
5. Plot the % cation meq/L on left ternary diagram; the % anion meq/L on the right.
6. Extrapolate into diamond field.

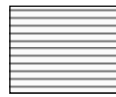
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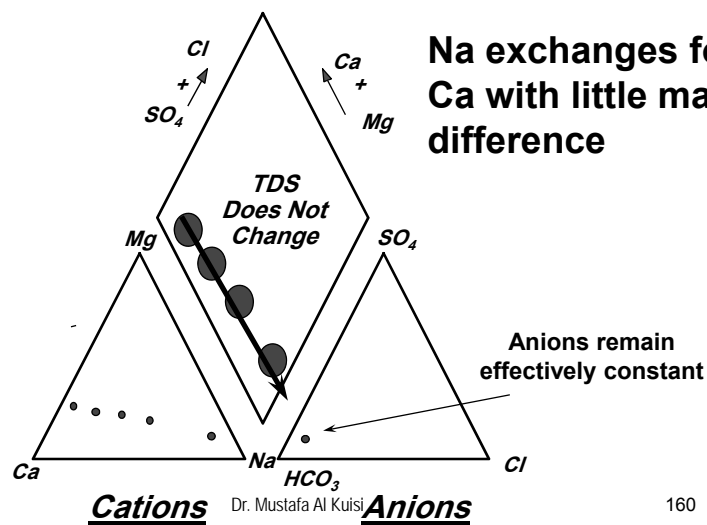




$$\text{Na-Clay} + \text{Ca}^{2+} = \text{Ca-Clay} + 2\text{Na}^{+}$$


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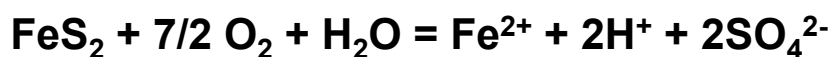
Na exchanges for Ca with little mass difference



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Sulfide Oxidation And Carbonate Dissolution...

Oxidation



Dissolving Limestone

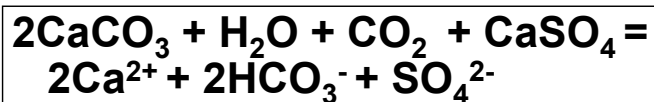


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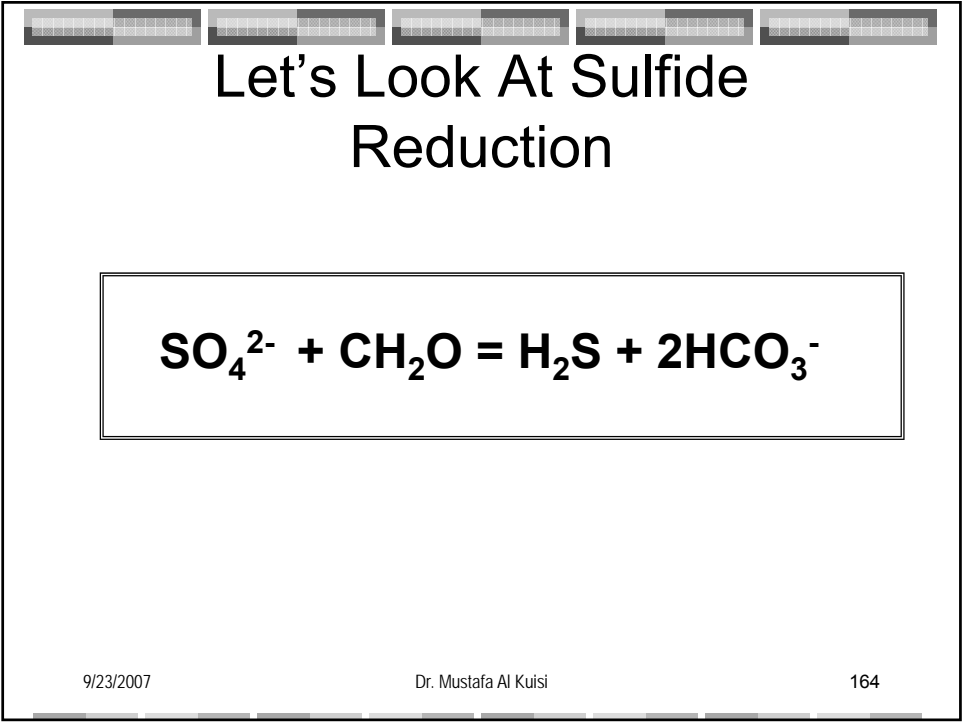
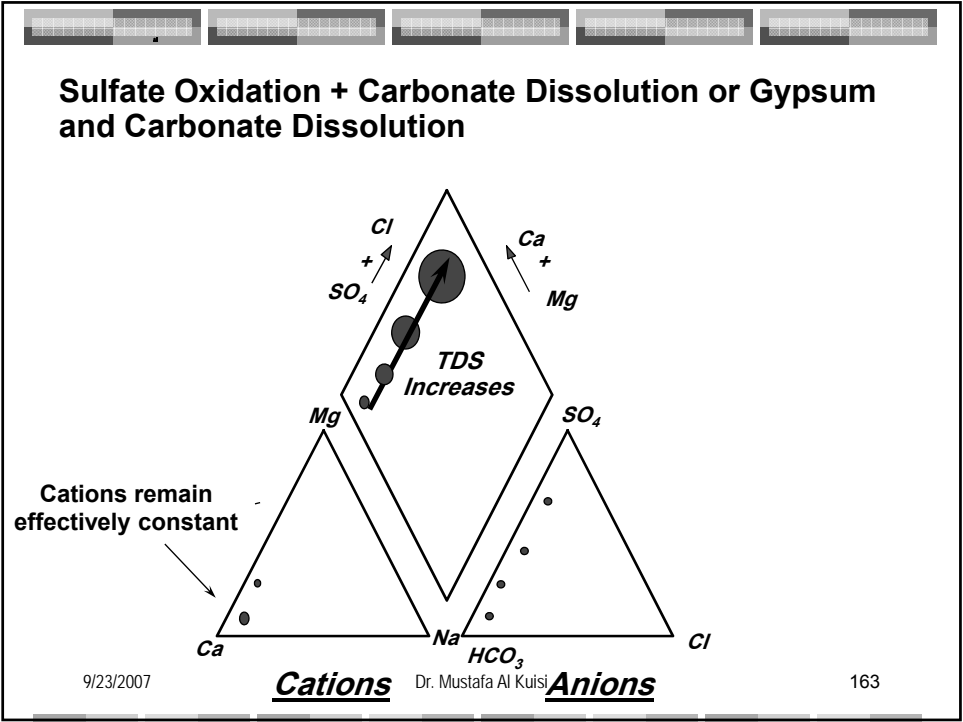
Sulfate and Carbonate Dissolution

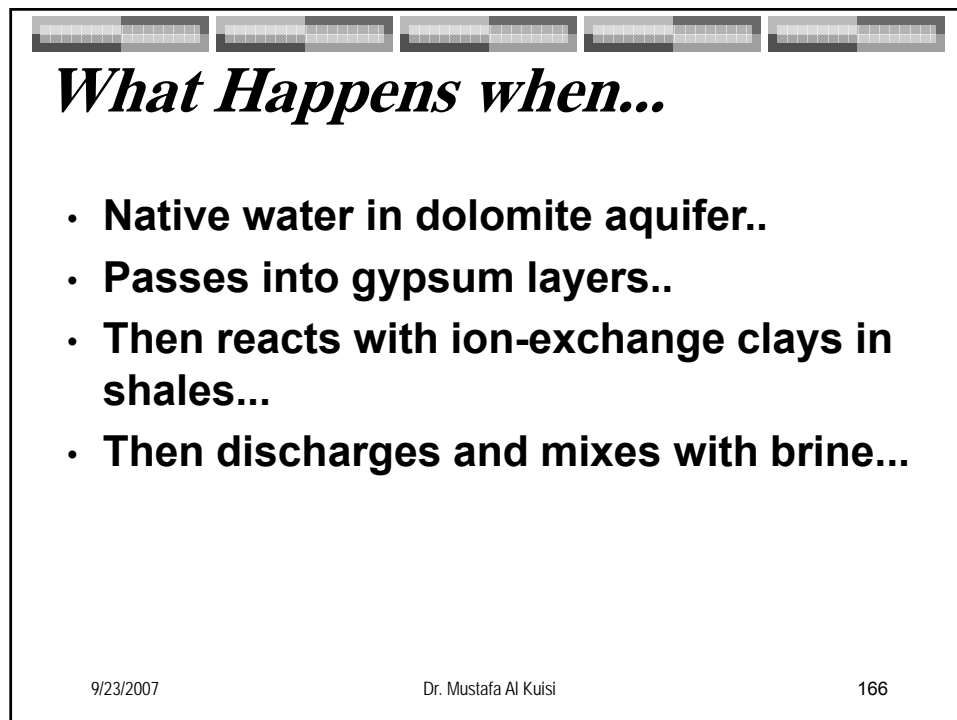
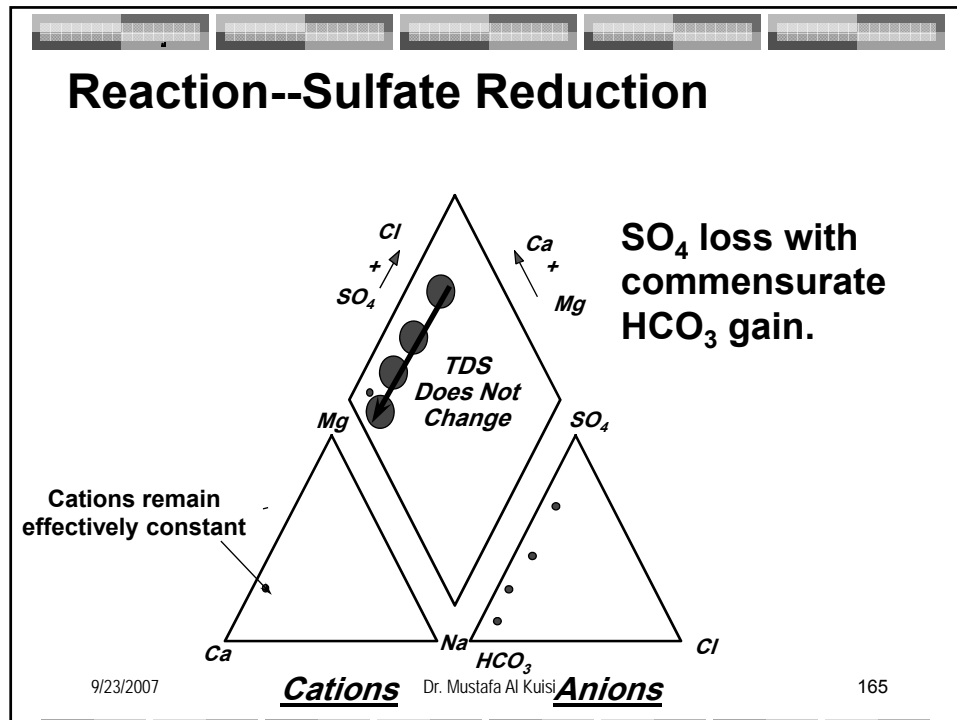


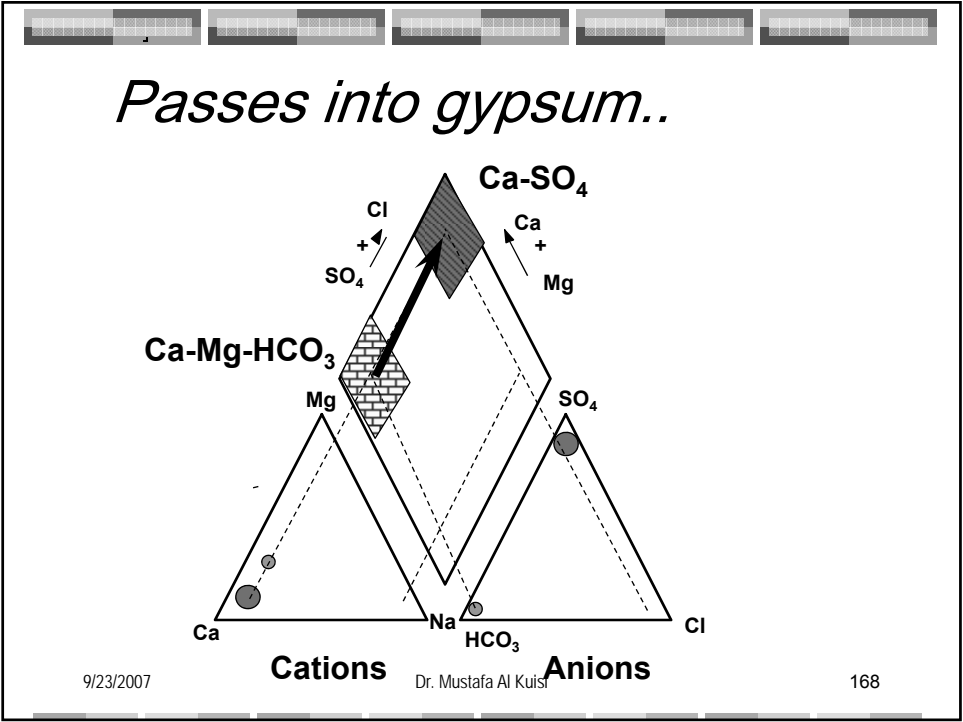
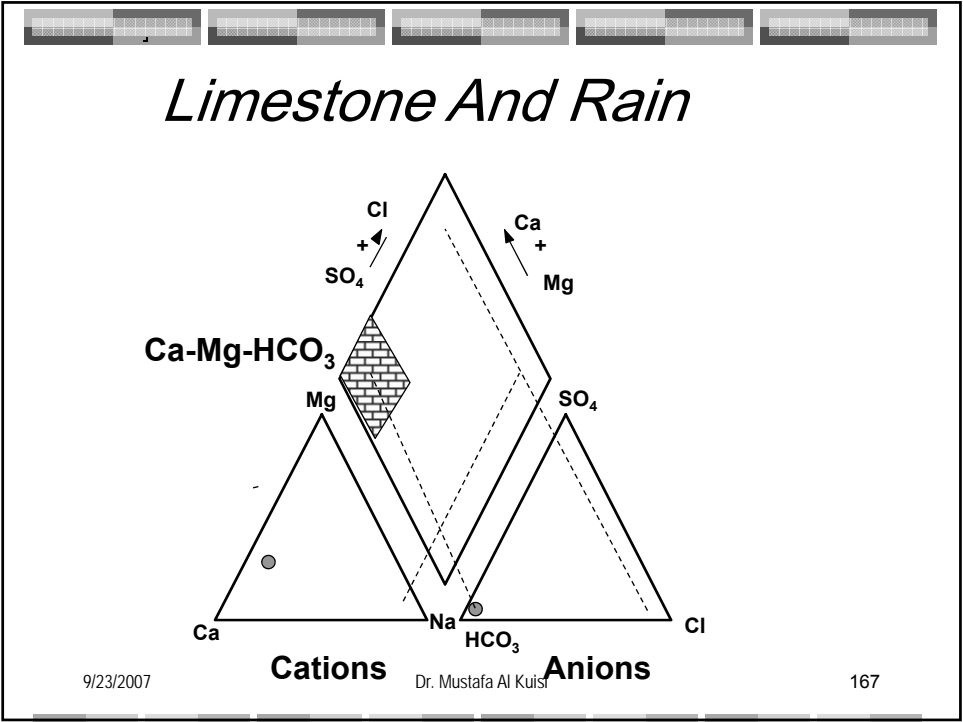
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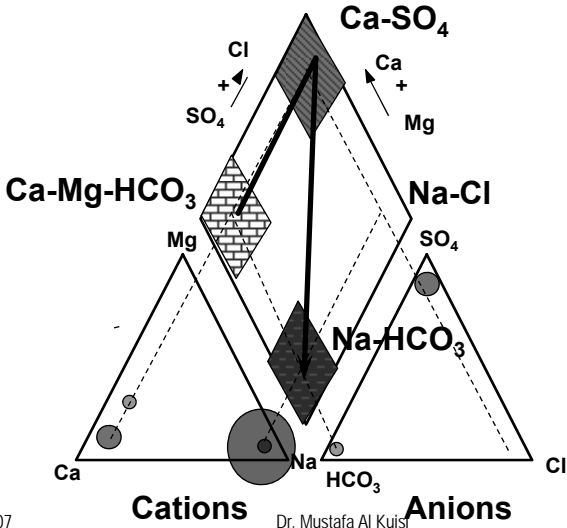
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Undergoes Ion Exchange..

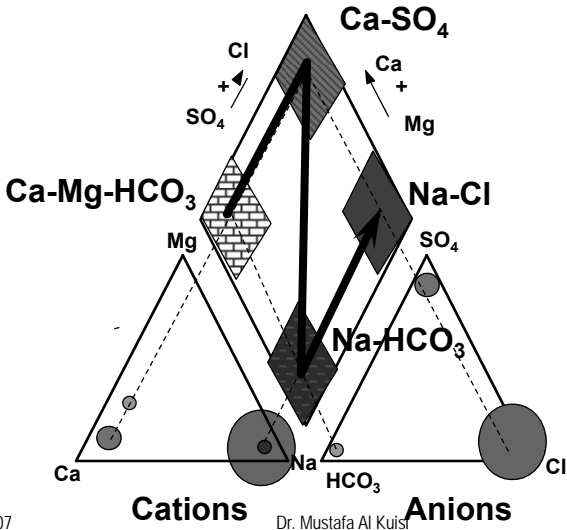


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Mixes with brine: The Mark of Zorro!!!!



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