

# Water Chemistry 2

## Sampling and Presenting Water Analyses

There is much to know and we only scratch the surface here. For more details see:

USGS document on Collection of Water Samples  
[http://water.usgs.gov/owq/FieldManual/chapter4/html/Ch4\\_contents.html](http://water.usgs.gov/owq/FieldManual/chapter4/html/Ch4_contents.html)

### AT THE SAMPLING SITE

November 8, 2007 11am

Date and time of water sampling

Sample #3

Location

MW33 near clear creek bridge

1 day after a major rain storm

Weather conditions at the time and, if appropriate, recent weather conditions

Well head is rusty

8" diam well TD132' WL32'

Purged 500 gal, >3 well vol

Air Temp = 58F

Water Temp = 50F

Conductivity = 875  $\mu\text{S}/\text{cm}$

pH = 9

Condition, for example, is there any debris? For surface water are there fish or plants in the water? Is there a lot of algae? For well samples document condition of well head and volume purged from the bore before taking the sample.

Any other observations that you think are interesting or significant (odors, color).

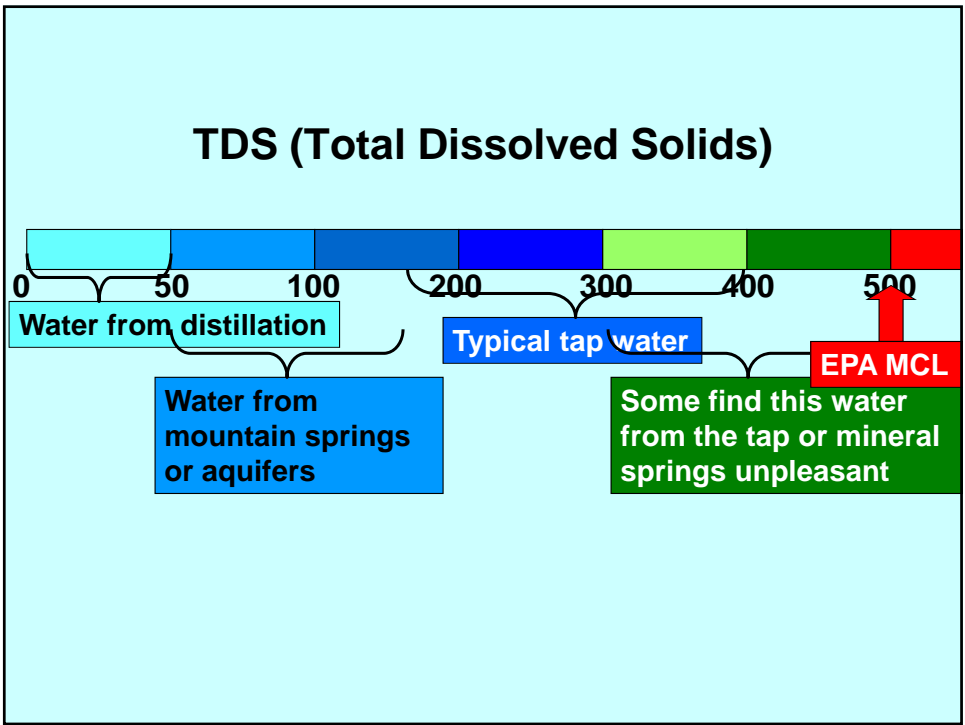
~ MW33 near clear creek bridge  
 1 day after a major rain storm  
 Well head is rusty  
 8" diam well TD132' WL32'  
 Purged 500 gal, >3 well vol  
 Air Temp = 58F  
 Water Temp = 50F  
 Conductivity = 875  $\mu$ S/cm  
 pH = 9  
 TDS?

**EPA Secondary Std  
MCL for  
TDS is 500 mg/L**

**A quick rough estimate of water quality  
Total Dissolved Solids**

**TDS in the lab:**  
weigh a vessel, add water sample, evaporate, note increased weight

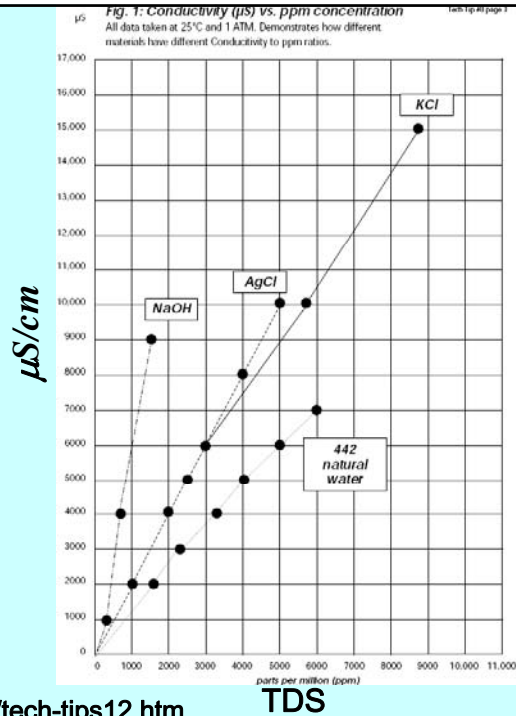
**In the field** we measure **Electrical Conductivity** ... the ability to carry electric current, which is carried by dissolved ions  
Some meters use a function to convert conductivity to TDS





Different materials have different Conductivity / TDS ratios

Note conductivity is temperature dependent so record T to allow adjusting conductivity



<http://www.eutechinst.com/techtips/tech-tips12.htm>

### Some example Conductivities and TDS values

|                   | Conductivity<br>µS/cm | TDS     |
|-------------------|-----------------------|---------|
| Divide Lake       | 10                    | 4.6     |
| Lake Superior     | 97                    | 63      |
| Lake Tahoe        | 92                    | 64      |
| Grindstone Lake   | 95                    | 65      |
| Ice Lake          | 110                   | 79      |
| Lake Independence | 316                   | 213     |
| Lake Mead         | 850                   | 640     |
| Atlantic Ocean    | 43,000                | 35,000  |
| Great Salt Lake   | 158,000               | 230,000 |

Fresh waters  
TDS < 1,000 mg/L

Saline waters  
TDS > ~ 35,000 mg/L

## How do we check correctness of analyses?

| Solute                        | Measured Conc (mg/L) |
|-------------------------------|----------------------|
| Ca <sup>2+</sup>              | 92.0                 |
| Mg <sup>2+</sup>              | 34.0                 |
| Na <sup>+</sup>               | 8.2                  |
| K <sup>+</sup>                | 1.4                  |
| Fe(III)                       | 0.1                  |
| HCO <sub>3</sub> <sup>-</sup> | 325.0                |
| SO <sub>4</sub> <sup>2-</sup> | 84.0                 |
| Cl <sup>-</sup>               | 9.6                  |
| NO <sub>3</sub> <sup>-</sup>  | 13.0                 |

### 1. Compare Measured TDS and Calculated TDS

**NOTE:**

When calculating TDS we group the mass of some items and call it Alkalinity

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

We will talk more about Alkalinity in the next lecture

### 2. Calculate Charge Balance

## Check Correctness of Analysis: Calculate TDS

| Solute                        | Measured Conc (mg/L) |
|-------------------------------|----------------------|
| Ca <sup>2+</sup>              | 92.0                 |
| Mg <sup>2+</sup>              | 34.0                 |
| Na <sup>+</sup>               | 8.2                  |
| K <sup>+</sup>                | 1.4                  |
| Fe(III)                       | 0.1                  |
| HCO <sub>3</sub> <sup>-</sup> | 325.0                |
| SO <sub>4</sub> <sup>2-</sup> | 84.0                 |
| Cl <sup>-</sup>               | 9.6                  |
| NO <sub>3</sub> <sup>-</sup>  | 13.0                 |

Calculated TDS =

$$0.6\text{Alkalinity} + \text{Na} + \text{K} + \text{Ca} + \text{Mg} + \text{Cl} + \text{SO}_4 + \text{SiO}_2 + \text{NO}_3\text{-N} + \text{F}$$

What is the Alkalinity?

What is the Calculated TDS?

Measured TDS > Calculated TDS because some species are not included in the calculation (e.g. Fe(III))

acceptable range:

$$1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$$

**If the ratio is out of the range,  
constituents should be reanalyzed**

Measured value in this case 603.5 mg/L

What is the ratio? Is it acceptable?

## Check Correctness of Analysis: Calculate Charge Balance

### 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 <sup>2+</sup>              | 92.0                  |                  |                   |                  |       |
| Mg <sup>2+</sup>              | 34.0                  |                  |                   |                  |       |
| Na <sup>+</sup>               | 8.2                   |                  |                   |                  |       |
| K <sup>+</sup>                | 1.4                   |                  |                   |                  |       |
| Fe(III)                       | 0.1                   |                  |                   |                  |       |
| HCO <sub>3</sub> <sup>-</sup> | 325.0                 |                  |                   |                  |       |
| SO <sub>4</sub> <sup>2-</sup> | 84.0                  |                  |                   |                  |       |
| Cl <sup>-</sup>               | 9.6                   |                  |                   |                  |       |
| NO <sub>3</sub> <sup>-</sup>  | 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




### Let's check the cation/anion balance

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



|  |   |  |                                       |   |  |   |                                     |
|--|---|--|---------------------------------------|---|--|---|-------------------------------------|
| 1<br><b>H</b><br>Hydrogen<br>1.00794   | 2<br><b>He</b><br>Helium<br>4.002602    |  |                                       |   |  |   |                                     |
| 3<br><b>Li</b><br>Lithium<br>6.941     | 4<br><b>Be</b><br>Beryllium<br>9.012182 | 5<br><b>B</b><br>Boron<br>10.811         | 6<br><b>C</b><br>Carbon<br>12.0107    | 7<br><b>N</b><br>Nitrogen<br>14.00674     | 8<br><b>O</b><br>Oxygen<br>15.9994     | 9<br><b>F</b><br>Fluorine<br>18.9984032 | 10<br><b>Ne</b><br>Neon<br>20.1797  |
| 11<br><b>Na</b><br>Sodium<br>22.989770 | 12<br><b>Mg</b><br>Magnesium<br>24.3050 | 13<br><b>Al</b><br>Aluminum<br>26.981538 | 14<br><b>Si</b><br>Silicon<br>28.0855 | 15<br><b>P</b><br>Phosphorus<br>30.973761 | 16<br><b>S</b><br>Sulfur<br>32.066     | 17<br><b>Cl</b><br>Chlorine<br>35.4527  | 18<br><b>Ar</b><br>Argon<br>39.948  |
| 19<br><b>K</b><br>Potassium<br>39.0983 | 20<br><b>Ca</b><br>Calcium<br>40.078    | 31<br><b>Ga</b><br>Gallium<br>69.723     | 32<br><b>Ge</b><br>Germanium<br>72.61 | 33<br><b>As</b><br>Arsenic<br>74.92160    | 34<br><b>Se</b><br>Selenium<br>78.96   | 35<br><b>Br</b><br>Bromine<br>79.904    | 36<br><b>Kr</b><br>Krypton<br>83.80 |
| 37<br><b>Rb</b><br>Rubidium<br>85.4678 | 38<br><b>Sr</b><br>Strontium<br>87.62   | 49<br><b>In</b><br>Indium<br>114.818     | 50<br><b>Sn</b><br>Tin<br>118.710     | 51<br><b>Sb</b><br>Antimony<br>121.760    | 52<br><b>Te</b><br>Tellurium<br>127.60 | 53<br><b>I</b><br>Iodine<br>126.90447   | 54<br><b>Xe</b><br>Xenon<br>131.29  |
| 55<br><b>Cs</b><br>Cesium<br>132.90545 | 56<br><b>Ba</b><br>Barium<br>137.327    | 81<br><b>Tl</b><br>Thallium<br>204.3833  | 82<br><b>Pb</b><br>Lead<br>207.2      | 83<br><b>Bi</b><br>Bismuth<br>208.98038   | 84<br><b>Po</b><br>Polonium<br>(209)   | 85<br><b>At</b><br>Astatine<br>(210)    | 86<br><b>Rn</b><br>Radon<br>(222)   |



**Check the cation/anion balance for this analysis:**

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

**What is the charge balance?**  
**Is it acceptable?**

## Summary checking correctness of analysis

### 1. Check Calculated vs Measured TDS

$$\frac{\text{measured TDS}}{\text{calculated TDS}} = \frac{603.5}{567.2} = 1.06$$

Between 1 and 1.2, so it's OK!

### 2. Check Anion-Cation (Charge) Balance

$$\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} = \frac{7.79 - 7.56}{7.79 + 7.56} = 0.0145$$

The cation/anion imbalance for the data is 1.5%  
< 5% so it's OK!

## What if there is an electrical imbalance?

### Possible reasons:

- The sampling program neglected to analyze for a major dissolved species. This may indicate a high concentration of an unusual anion or cation.
- Laboratory error - some serious systematic error occurred
- In certain cases the dissolved species of the element of a compound may not correspond to the typical species used in making the ion balance calculation.



## How do we present the analysis?

The options have advantages and disadvantages

Presentation formats:

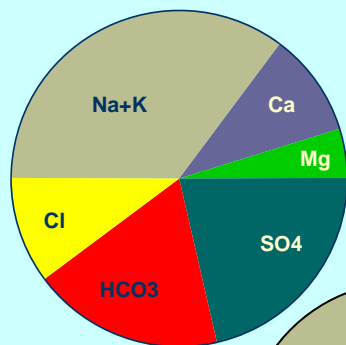
Abundance or Relative Abundance

- Pie Diagram
- Collins Diagram
- Schoeller Diagram
- Stiff Diagram
- Piper Diagram

Spatial Patterns

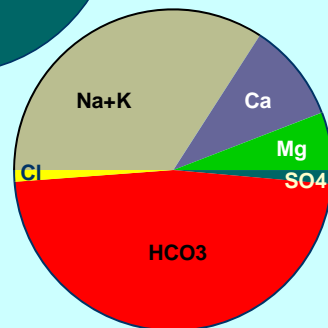
- Contours of individual constituents (often noisy)
- Abundance diagrams on a map

## PIE CHARTS



Display of concentration ratios for individual samples

Easier to compare concentration ratios for several different samples compared with a table of numbers

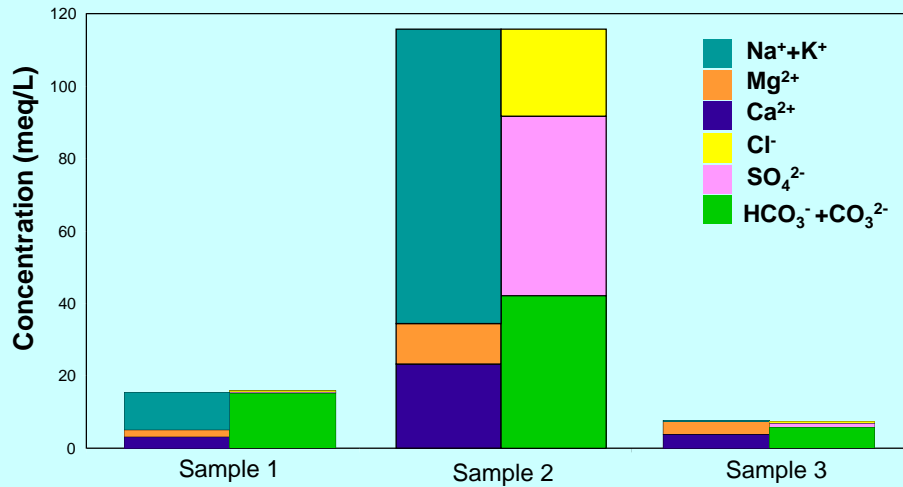


## COLLINS DIAGRAM

Display of concentrations (not ratios) for individual samples  
but as it is a cumulative chart the values are not readily apparent

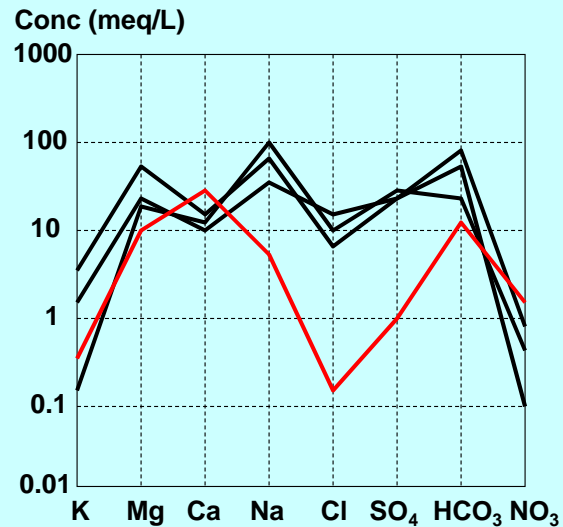
Total height ~ reflects TDS

Easier to compare samples than pie charts



## SCHOELLER DIAGRAM

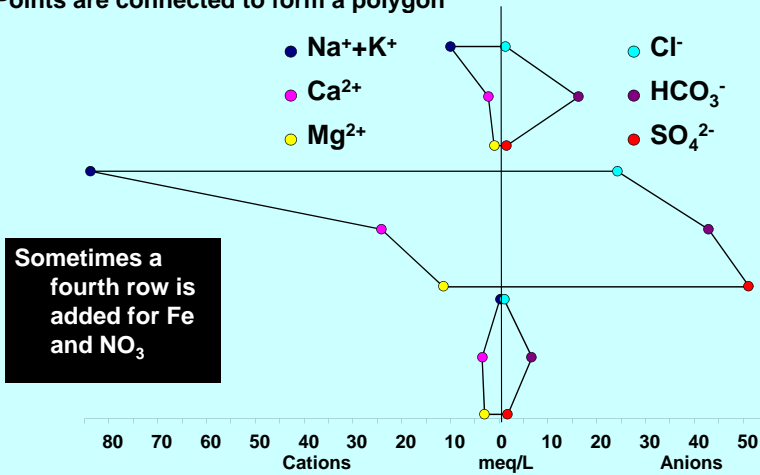
- Logarithmic diagrams of major ion analyses in meq/l demonstrate different water types on the same diagram
- Sample concentrations not ratios are displayed and compared
- Similar waters exhibit similar "fingerprints"



# STIFF DIAGRAM

Displays concentration ratios for individual samples  
 Shape makes it easier to compare samples  
 Especially if displayed on maps

Concentrations in meq/L are plotted on the horizontal axis  
 Cations on the left Anions on the right  
 Points are connected to form a polygon

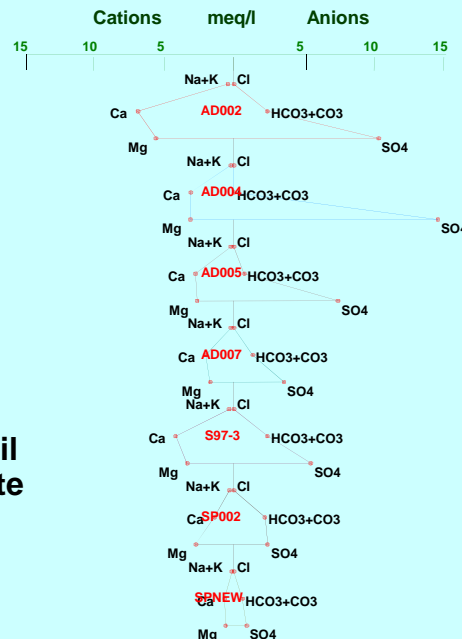


## Stiff Diagram Example

Na, K and Cl rarely extend horizontally beyond the vertical axis, so relatively unimportant in this area

Ca and Mg are the most important cations

Most samples have a long tail at the sulfate vertex, sulfate is the dominant anion



## PIPER DIAGRAMS

### ADVANTAGES

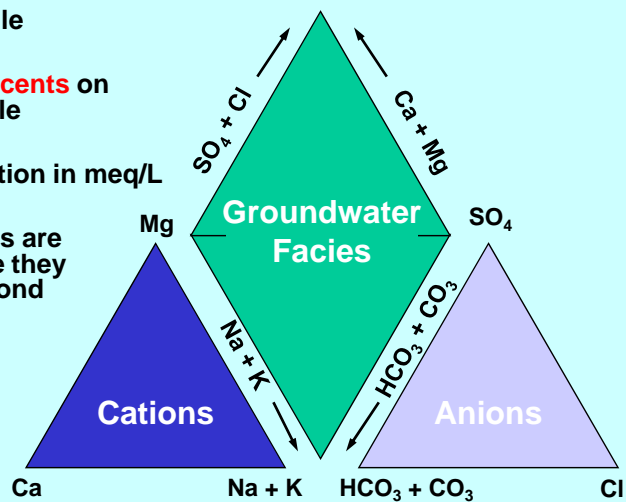
- Many water analyses can be plotted on the same diagram
- Can be used to classify waters
- Can be used to identify mixing of waters

### DISADVANTAGE

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

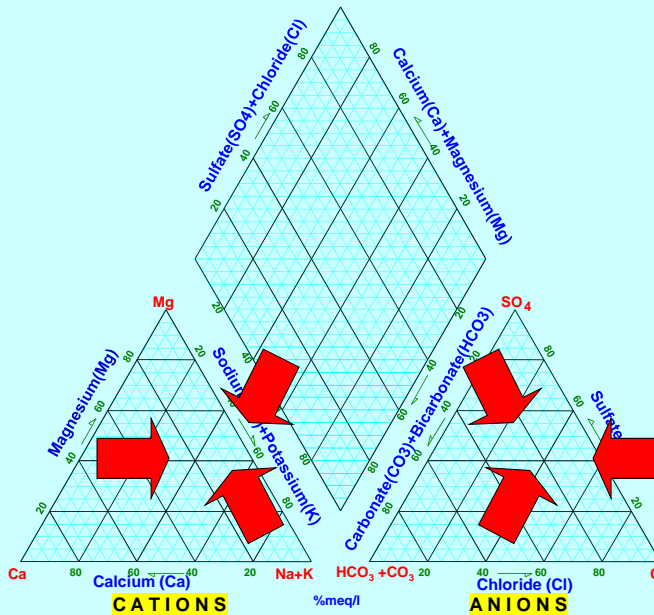
## PIPER DIAGRAM

- Two triangles (cations & anions) & Central diamond-shape (combined)
- Cations plotted as **percents** on Ca-Mg-(Na + K) triangle
- Anions plotted as **percents** on  $\text{HCO}_3^-$ - $\text{SO}_4^{2-}$ - $\text{Cl}^-$  triangle
- Percent of Concentration in meq/L
- Points on the triangles are projected up to where they intersect on the diamond



## Plotting on a Piper Diagram

|                               |           |
|-------------------------------|-----------|
| Ca                            | 40 ppm    |
| Mg                            | 15 ppm    |
| Na                            | 120 ppm   |
| K                             | 20 ppm    |
| HCO <sub>3</sub> <sup>-</sup> | 2.8 meq/L |
| SO <sub>4</sub>               | 234 ppm   |
| Cl                            | 45 ppm    |



## Plotting on a Piper Diagram

|                               |           |
|-------------------------------|-----------|
| Ca                            | 40 ppm    |
| Mg                            | 15 ppm    |
| Na                            | 120 ppm   |
| K                             | 20 ppm    |
| HCO <sub>3</sub> <sup>-</sup> | 2.8 meq/L |
| SO <sub>4</sub>               | 234 ppm   |
| Cl                            | 45 ppm    |

Convert to Equivalents / L  
Divide by formula weight  
Multiply by charge

|    |                        |                               |                       |
|----|------------------------|-------------------------------|-----------------------|
| Ca | $1.996 \times 10^{-3}$ | HCO <sub>3</sub> <sup>-</sup> | $2.8 \times 10^{-3}$  |
| Mg | $1.234 \times 10^{-3}$ | SO <sub>4</sub>               | $4.88 \times 10^{-3}$ |
| Na | $5.22 \times 10^{-3}$  | Cl                            | $1.27 \times 10^{-3}$ |
| K  | $0.51 \times 10^{-3}$  |                               |                       |

Sum Na+K

Normalize Ca Mg Na+K to 100%

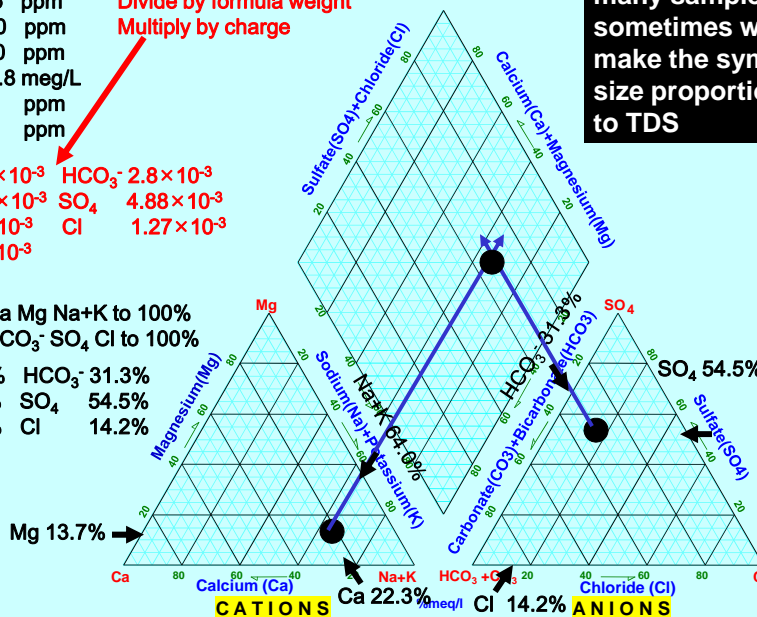
Normalize HCO<sub>3</sub><sup>-</sup> SO<sub>4</sub> Cl to 100%

Ca 22.3% HCO<sub>3</sub><sup>-</sup> 31.3%

Mg 13.7% SO<sub>4</sub> 54.5%

Na+K 64.0% Cl 14.2%

When plotting many samples sometimes we make the symbol size proportional to TDS



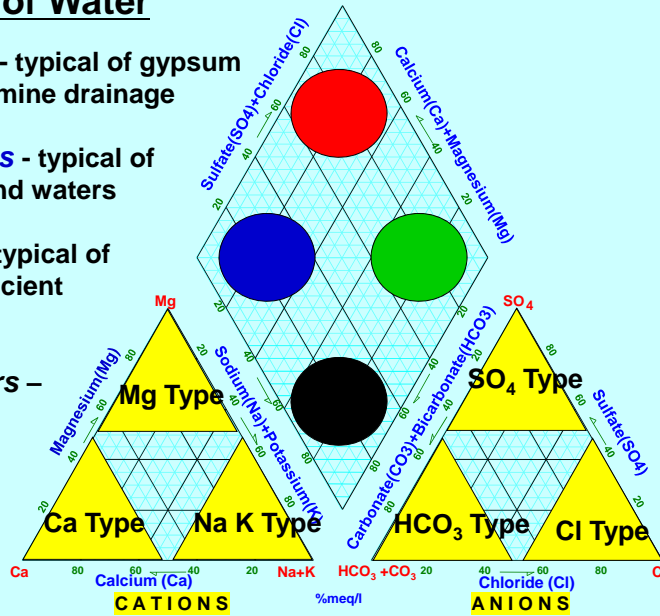
## Classification of Water

● **Ca-SO<sub>4</sub> waters** - typical of gypsum ground waters and mine drainage

● **Ca-HCO<sub>3</sub> waters** - typical of shallow, fresh ground waters

● **Na-Cl waters** - typical of marine and deep ancient ground waters

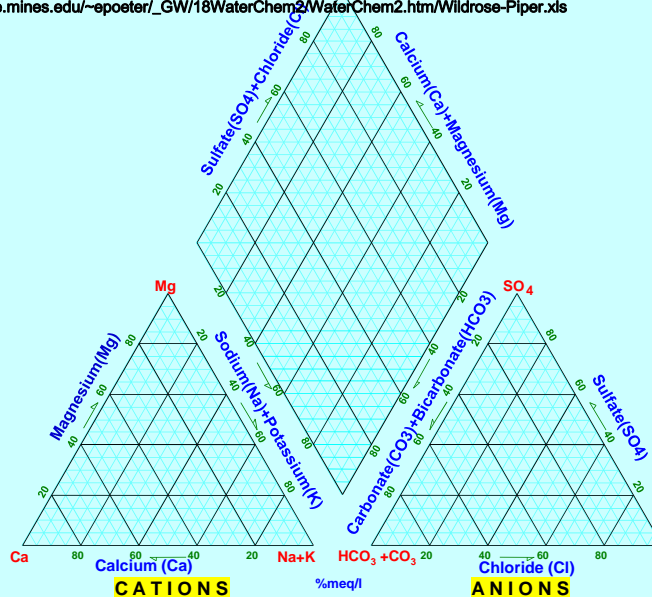
● **Na-HCO<sub>3</sub> waters** - typical of deeper ground waters influenced by ion exchange

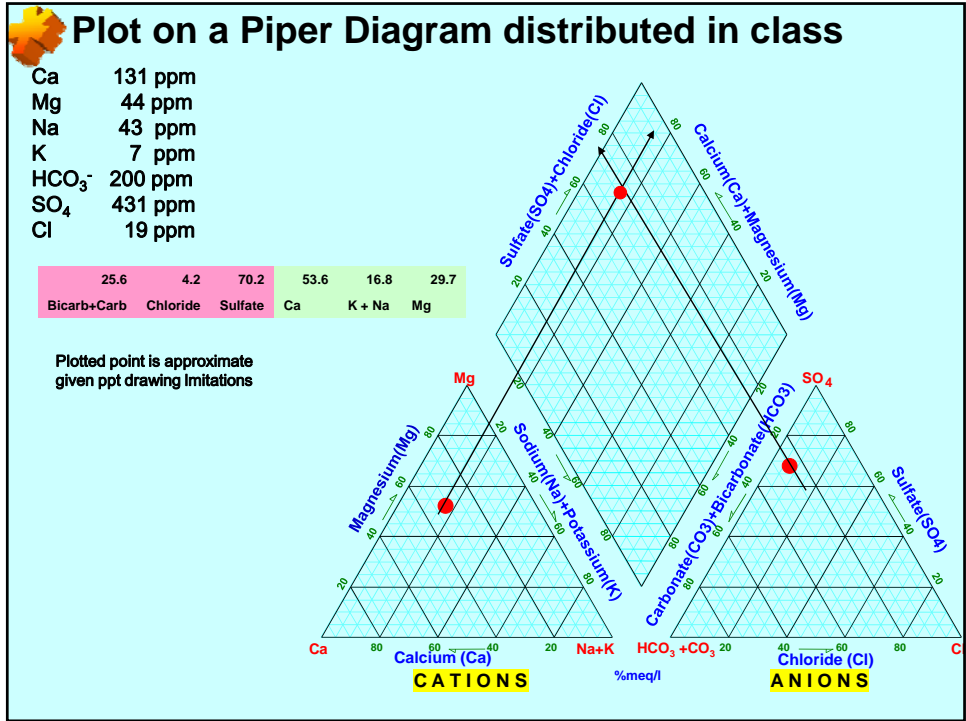


## Plot on a Piper Diagram distributed in class

|                               |         |
|-------------------------------|---------|
| Ca                            | 131 ppm |
| Mg                            | 44 ppm  |
| Na                            | 43 ppm  |
| K                             | 7 ppm   |
| HCO <sub>3</sub> <sup>-</sup> | 200 ppm |
| SO <sub>4</sub>               | 431 ppm |
| Cl                            | 19 ppm  |

If you want to download data in a spreadsheet, go to [http://inside.mines.edu/~eposter/\\_GW/18WaterChem2/WaterChem2.htm/Wildrose-Piper.xls](http://inside.mines.edu/~eposter/_GW/18WaterChem2/WaterChem2.htm/Wildrose-Piper.xls)





**Rockworks: software for visualizing, interpreting and presenting surface and subsurface data**  
<http://www.rockware.com>

Class data sets available for download on today's class page  
[http://inside.mines.edu/~epoeter/\\_GW/18WaterChem2/WaterChem2.htm](http://inside.mines.edu/~epoeter/_GW/18WaterChem2/WaterChem2.htm)  
 Maps  
 WaterChem2-data.zip

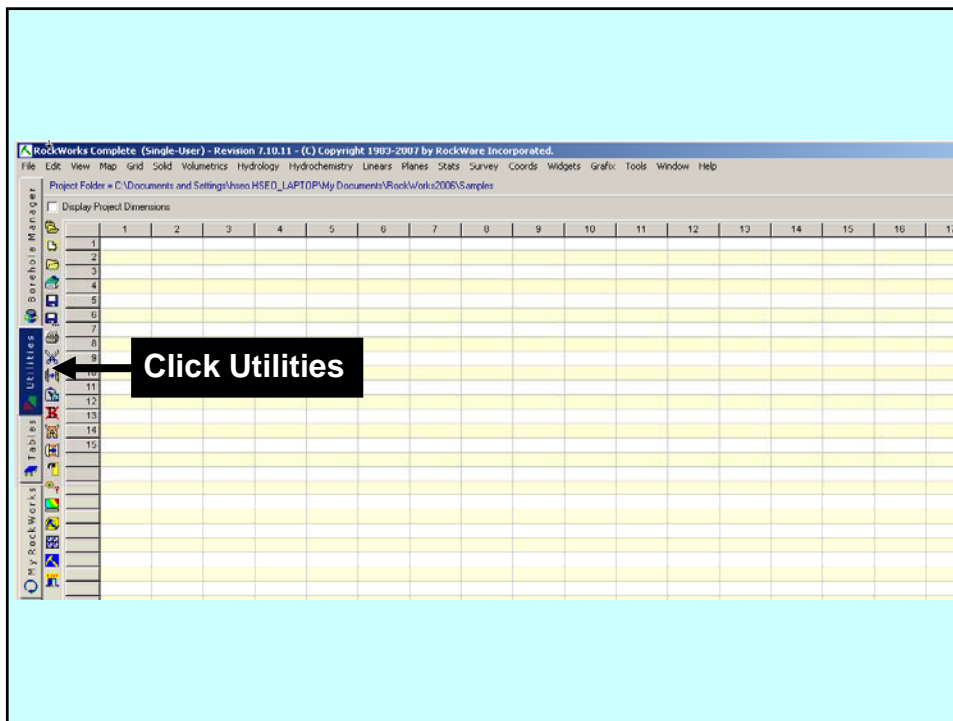
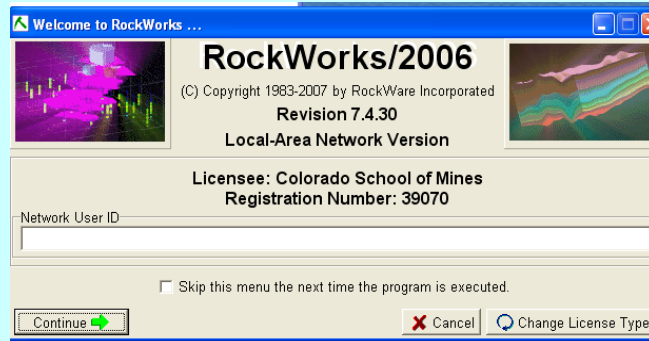
Download those files now

Unzip the zip file to a folder of your choice

You can choose to look at one of 2 data sets  
 Death Valley (source water identification) or  
 Ohio (water quality in a mining district)  
 xls files which you know how to create &  
 atd files from Rockworks which are simply the xls with symbols added in  
 rockworks and saved as an atd – I did this to save you the tedium

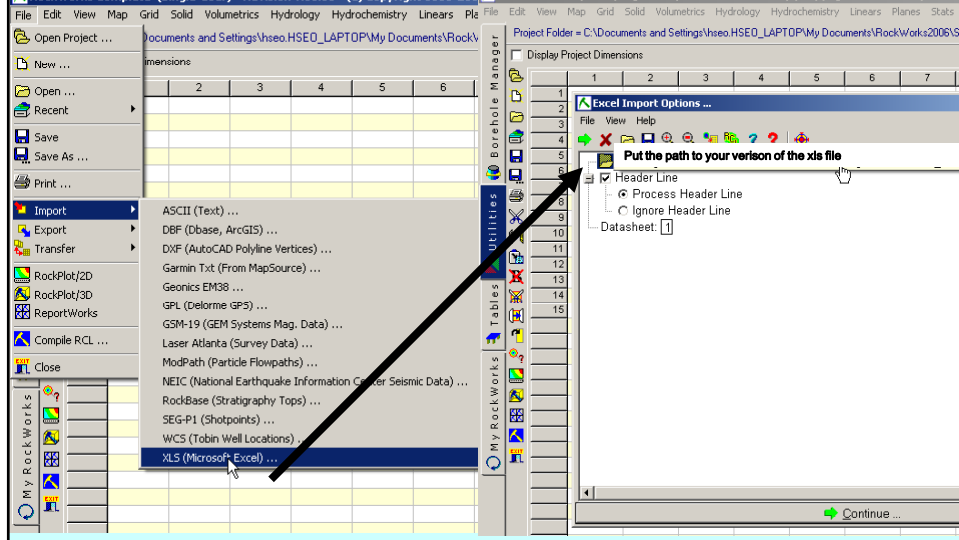
## RockWorks2006

- Launch RockWorks2006 (in the Geology applications)
- Under “Network User ID”, type your username & continue
- If you get a message about **UPDATING CANCEL IT**
- If it opens to a help page **XiT IT**





To import an xls File|Import|XLS, import data.xls yes, process header line  
 Afterward you will need to do a lot of set up, column titles, define symbols,  
 enter project range. I have done that for you in the atd files  
**SO for this exercise OPEN the rockware file I provided (\*.atd)**  
**Choose Death Valley or Ohio according to your interest**



Now go to Hydrochemistry

Experiment with ion balance, TDS calculation, Piper plot, Stiff diagram and (for Ohio where we have x,y,z) Stiff Maps

Watch the options

- \*\*\* Notice you will need to scan project dimensions if you are to make a map
- \*\*\* Notice when you select an analysis under hydrochemistry a bar appears on the left. Be sure to select the correct column headers on that bar. If there are no data for an item, choose and empty column. ALSO notice sometimes you need to select a column for the output of the analysis ... Be sure to choose an empty column (it is useful to label that column, right click on the column header for options).
- \*\*\* Note you may need to wait a bit for a plot or map to appear. Generally you know it is working because it reports progress on tasks on the lower bar.

Consider whether your outputs make sense

(make sure you could do these analyses without Rockware)

Note items to consider on the following slide



The sample data that you just plotted on the paper Piper diagram in class is one of the Death Valley samples, Wildrose Spring. Compare your plotted point to the one that Rockware plots.

Consider the Data with respect to the maps on the next two slides. (note: we will discuss these again in an upcoming class)

**HOMEWORK:**

Make an interesting observation using Rockworks on one of these data sets.

You must attach the associated Rockworks diagram and explain how it supports your observation

