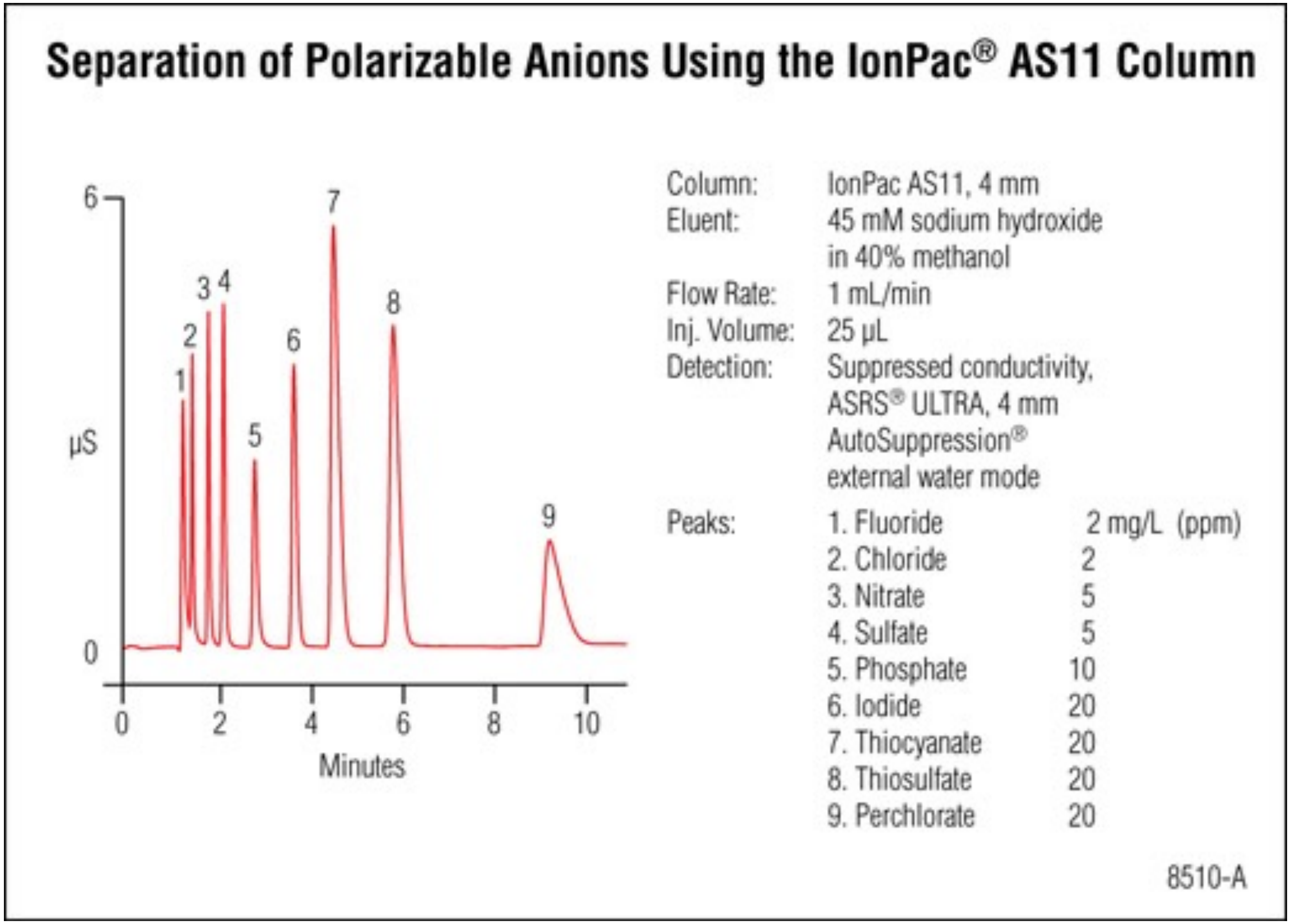
Data Analysis and Statistics

EAR 419/619 Aqueous Geochemistry

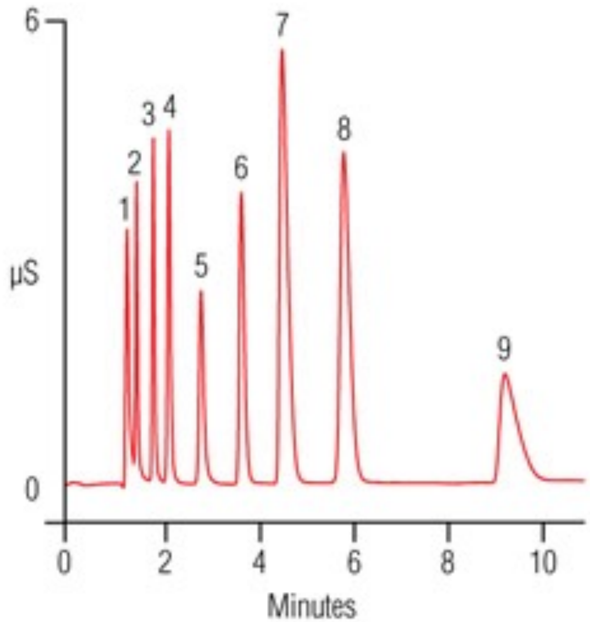
Lab 3

What does an instrument report?

- ***Raw data*** typically consists of instrument response values with units that depend on the method of detection used by the instrument (e.g., conductivity, absorbance)



Separation of Polarizable Anions Using the IonPac® AS11 Column



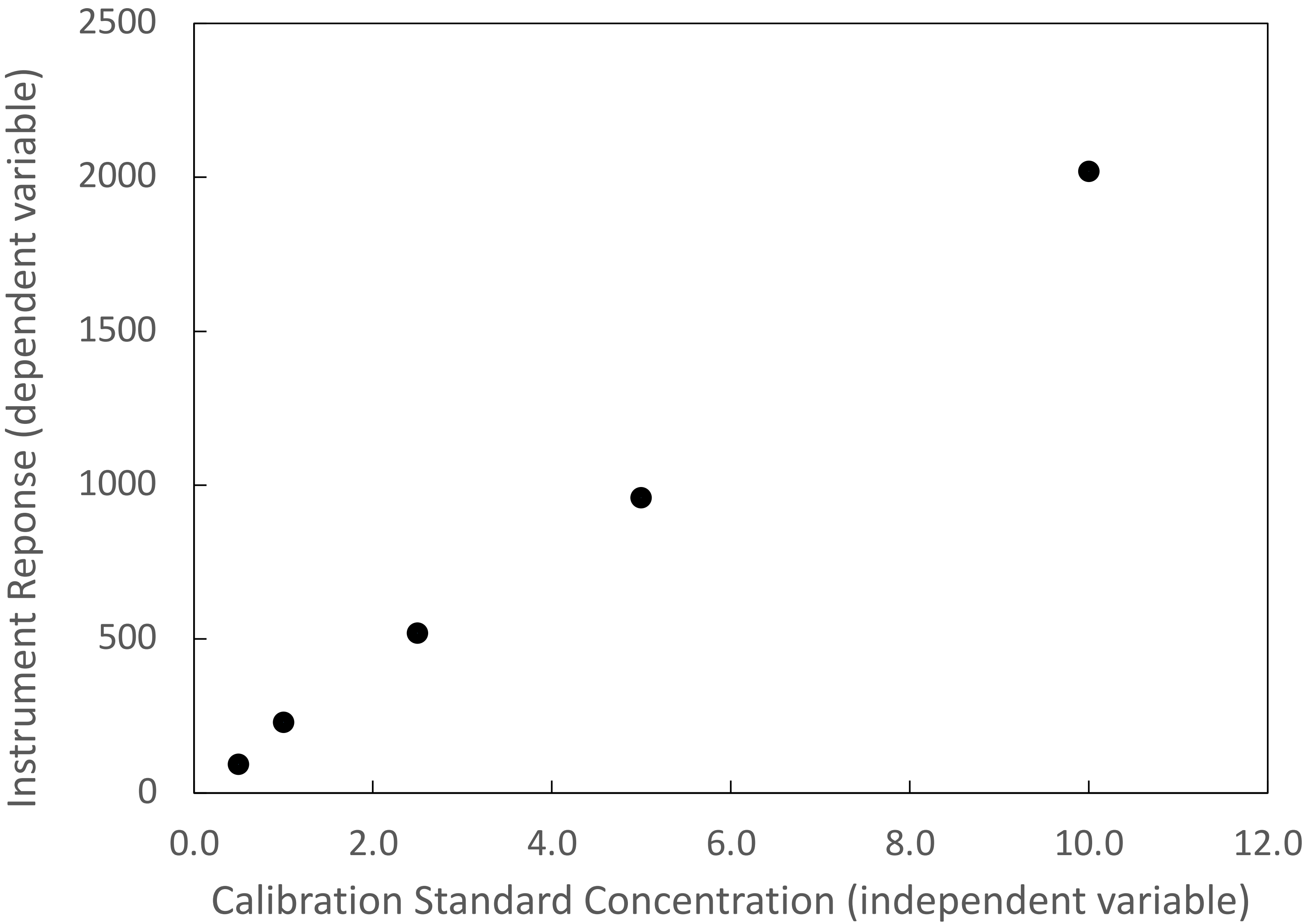
Column:	IonPac AS11, 4 mm	
Eluent:	45 mM sodium hydroxide in 40% methanol	
Flow Rate:	1 mL/min	
Inj. Volume:	25 µL	
Detection:	Suppressed conductivity, ASRS® ULTRA, 4 mm AutoSuppression® external water mode	
Peaks:	1. Fluoride	2 mg/L (ppm)
	2. Chloride	2
	3. Nitrate	5
	4. Sulfate	5
	5. Phosphate	10
	6. Iodide	20
	7. Thiocyanate	20
	8. Thiosulfate	20
	9. Perchlorate	20

8510-A

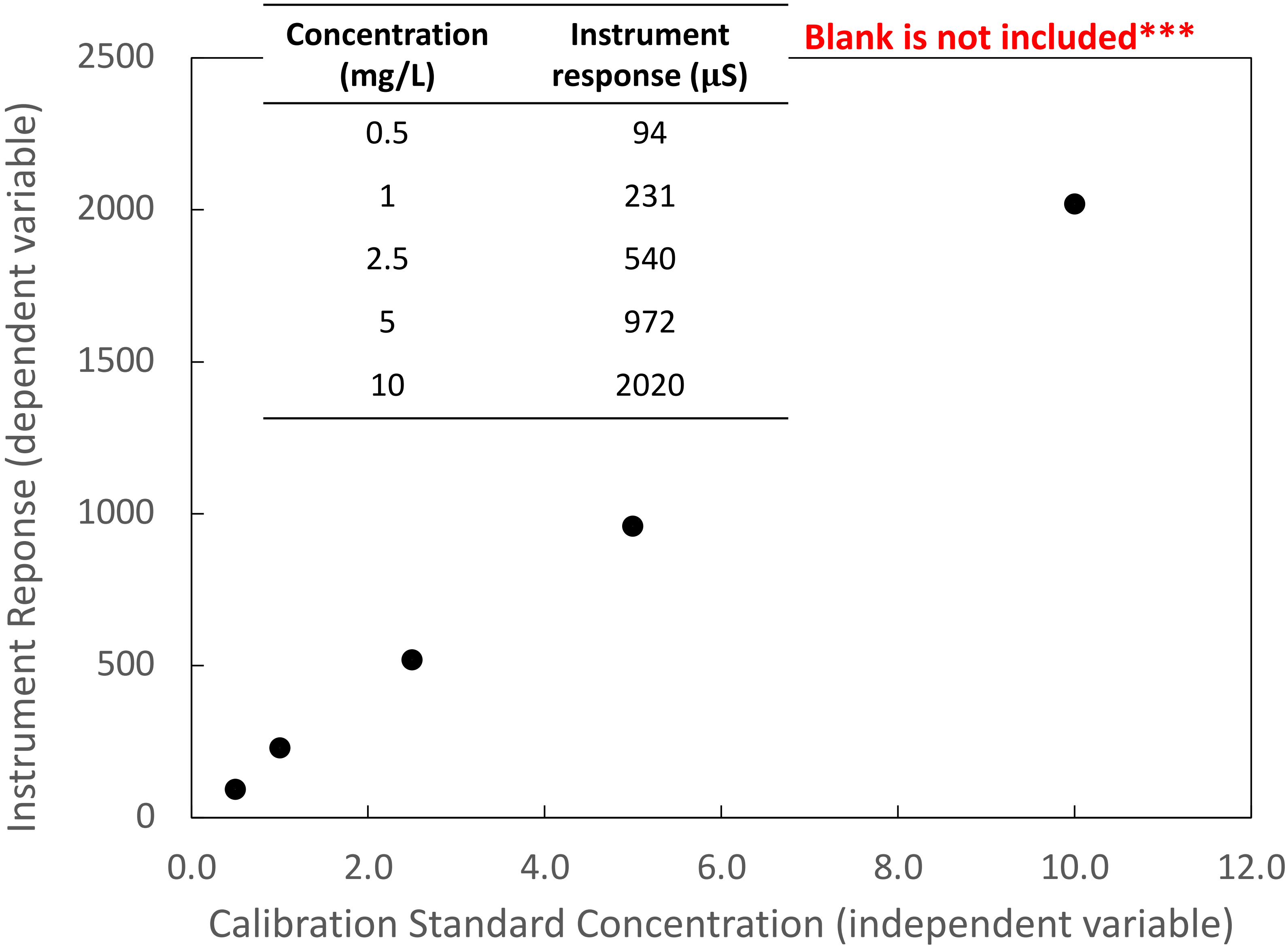
Ion chromatography:
raw data = area under the peak

- Measured as µS*min

Raw data are converted to concentration values using a *calibration curve*

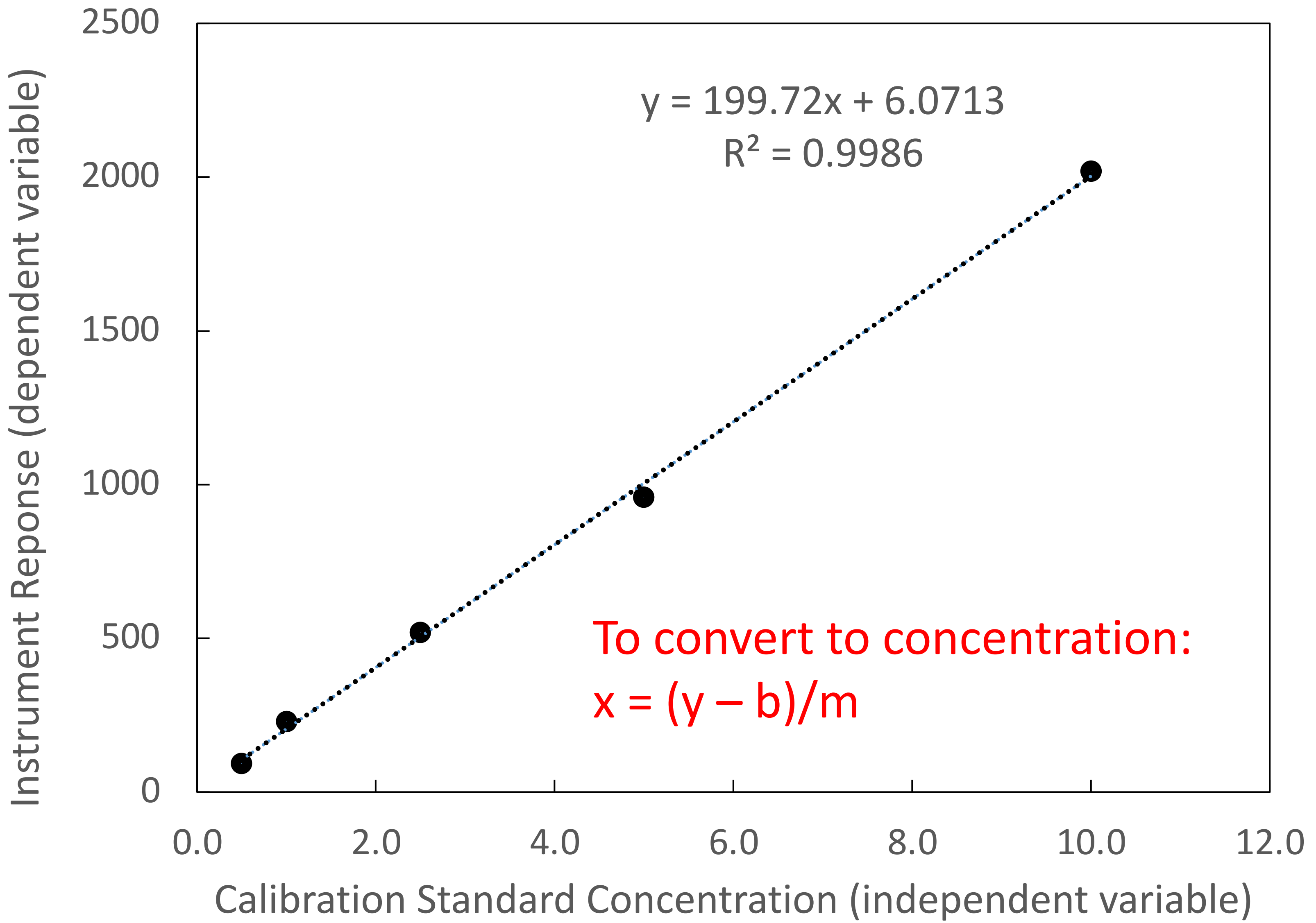


Calibration curves are constructed by measuring instrument response to solutions of known concentration (calibration standards)

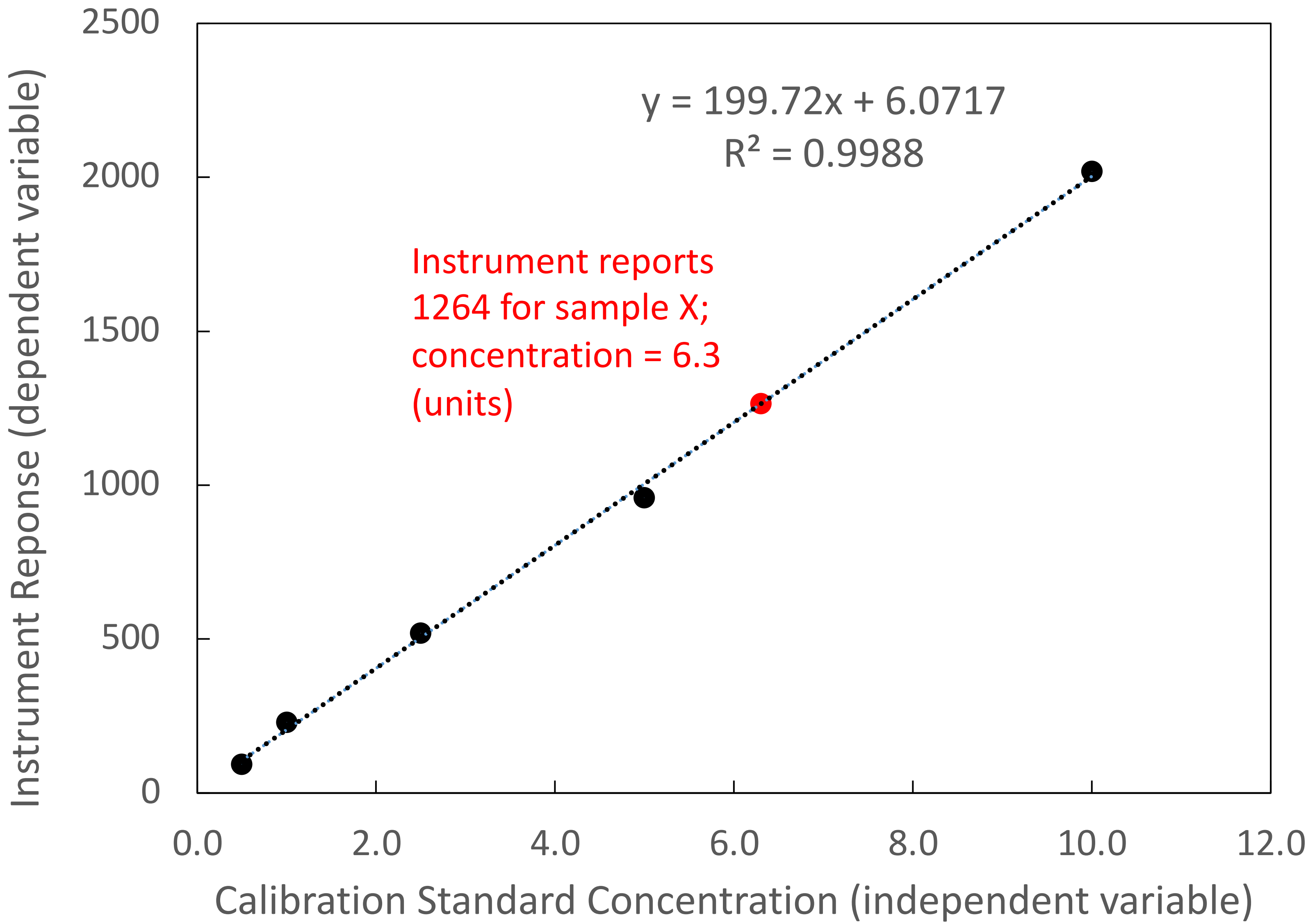


Concentration (mg/L)	Instrument response (µS)
0.5	94
1	231
2.5	540
5	972
10	2020

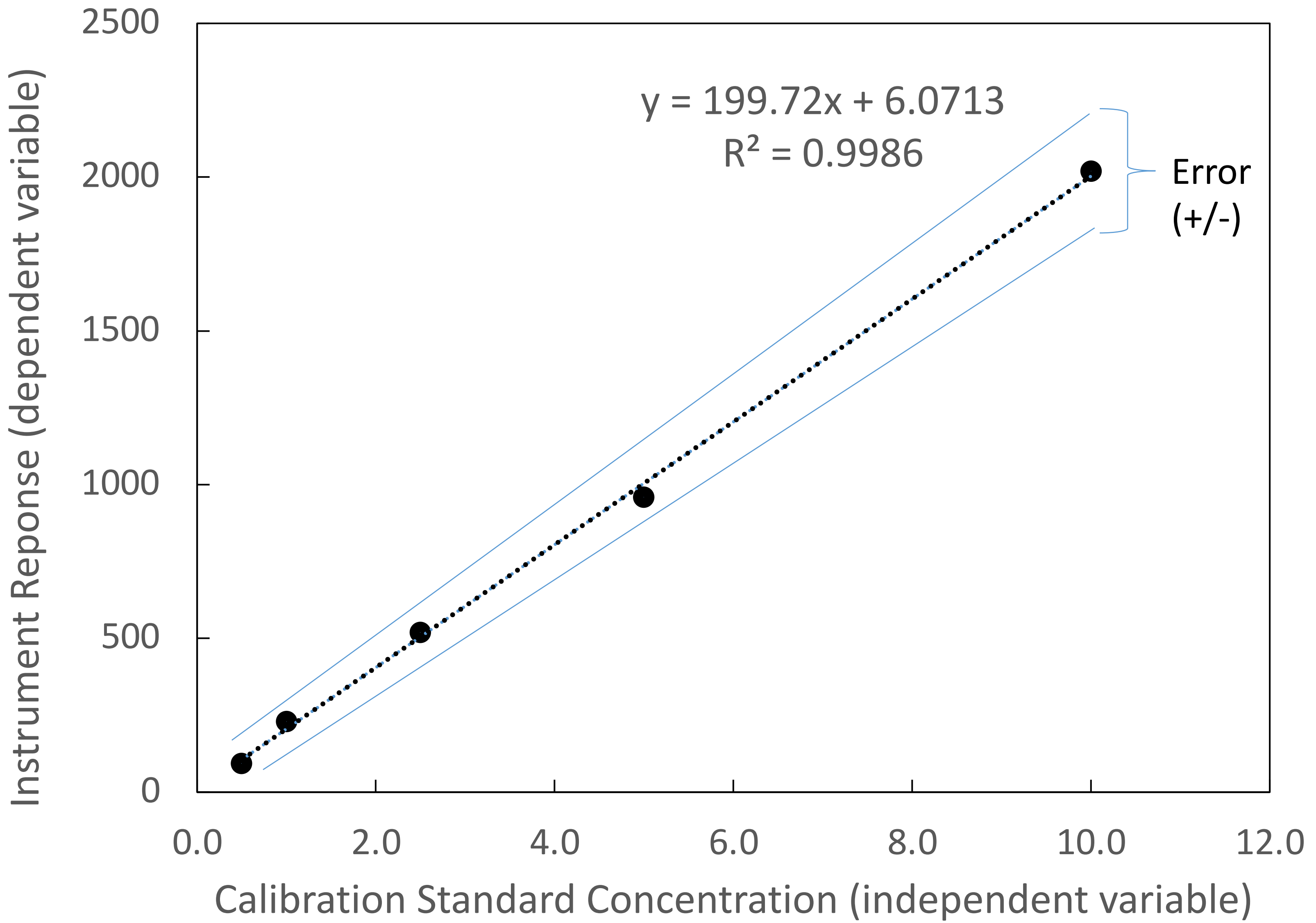
Linear regression is used to derive the relationship between x and y-values in order to calculate unknown concentrations from the raw data measured on the instrument



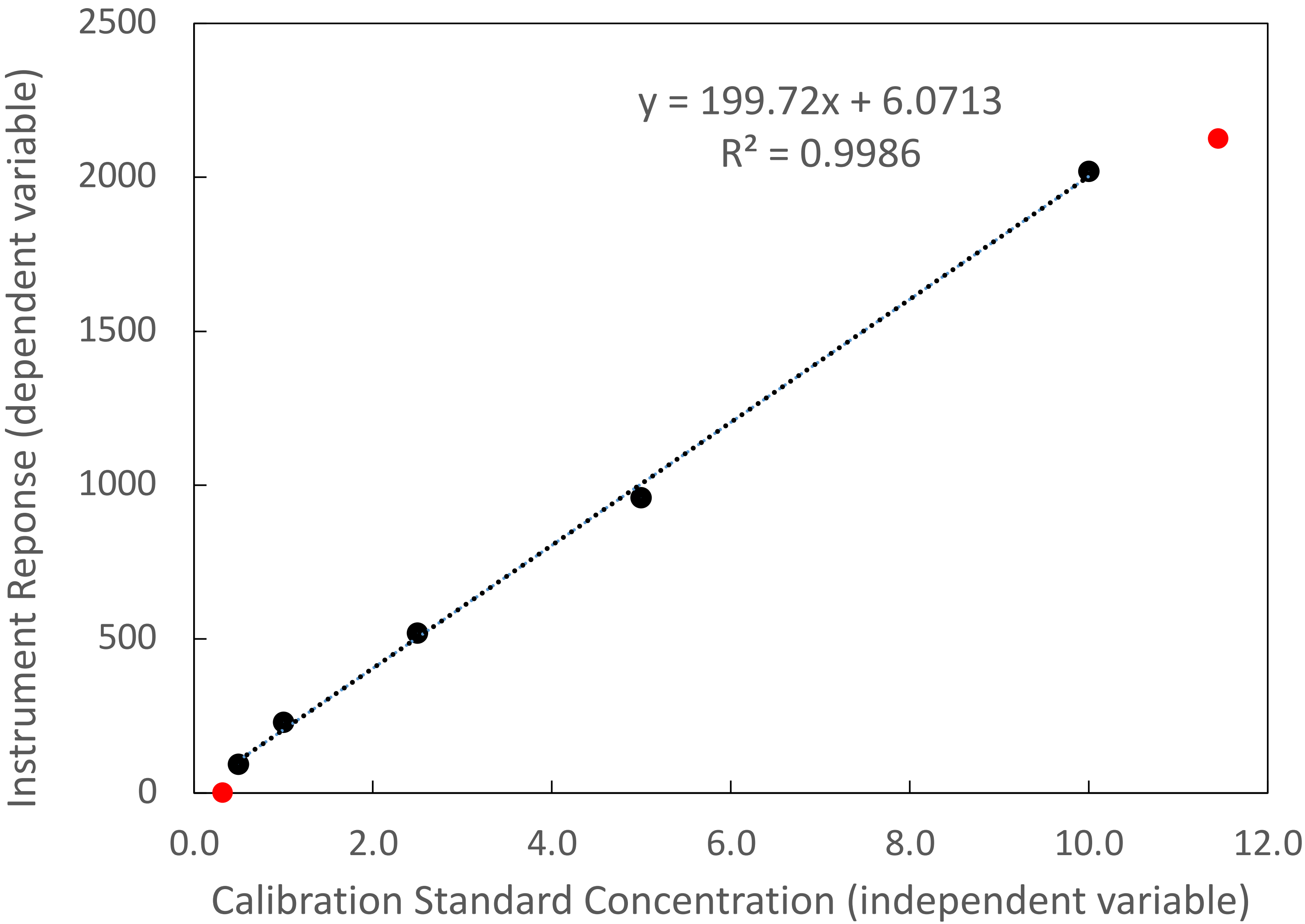
Samples are best quantifiable within the calibration range



The calibration curve can be used to calculate analytical error (details in lab handout)



Samples are best quantifiable within the calibration range



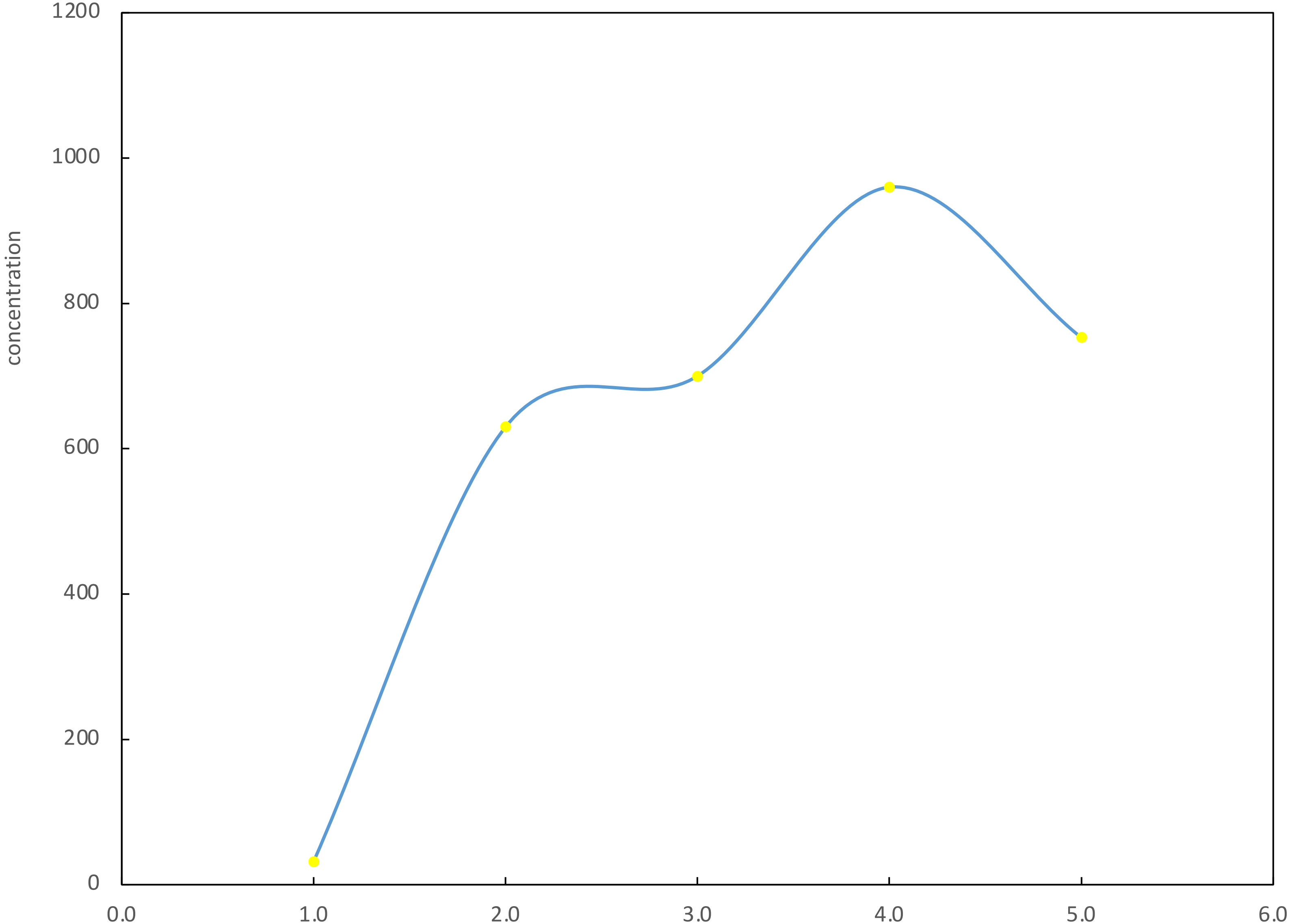
Data Visualization

What are the properties of a good figure?

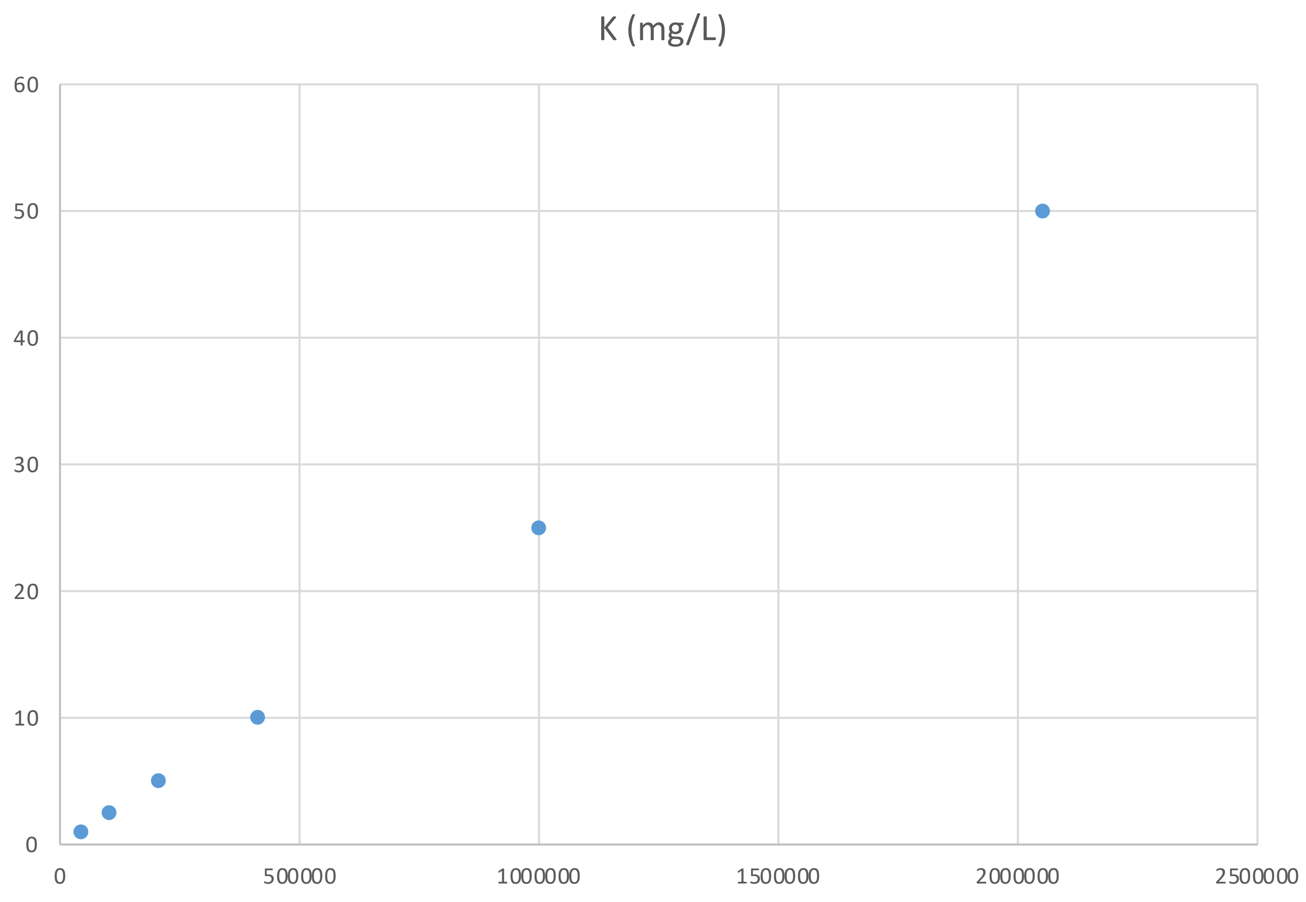
The purpose of a figure is to visually display results in a way that best communicates information to the reader

- gives all necessary information (e.g., titles, units)
- highlights important trends (similarity or dissimilarity between sets of data points
- Clear and easy to read: large text, simple font, large symbols, high contrast
- Figures <u>need</u> axes, axes labels with units; figure titles and grids are not needed

How can we improve this figure?

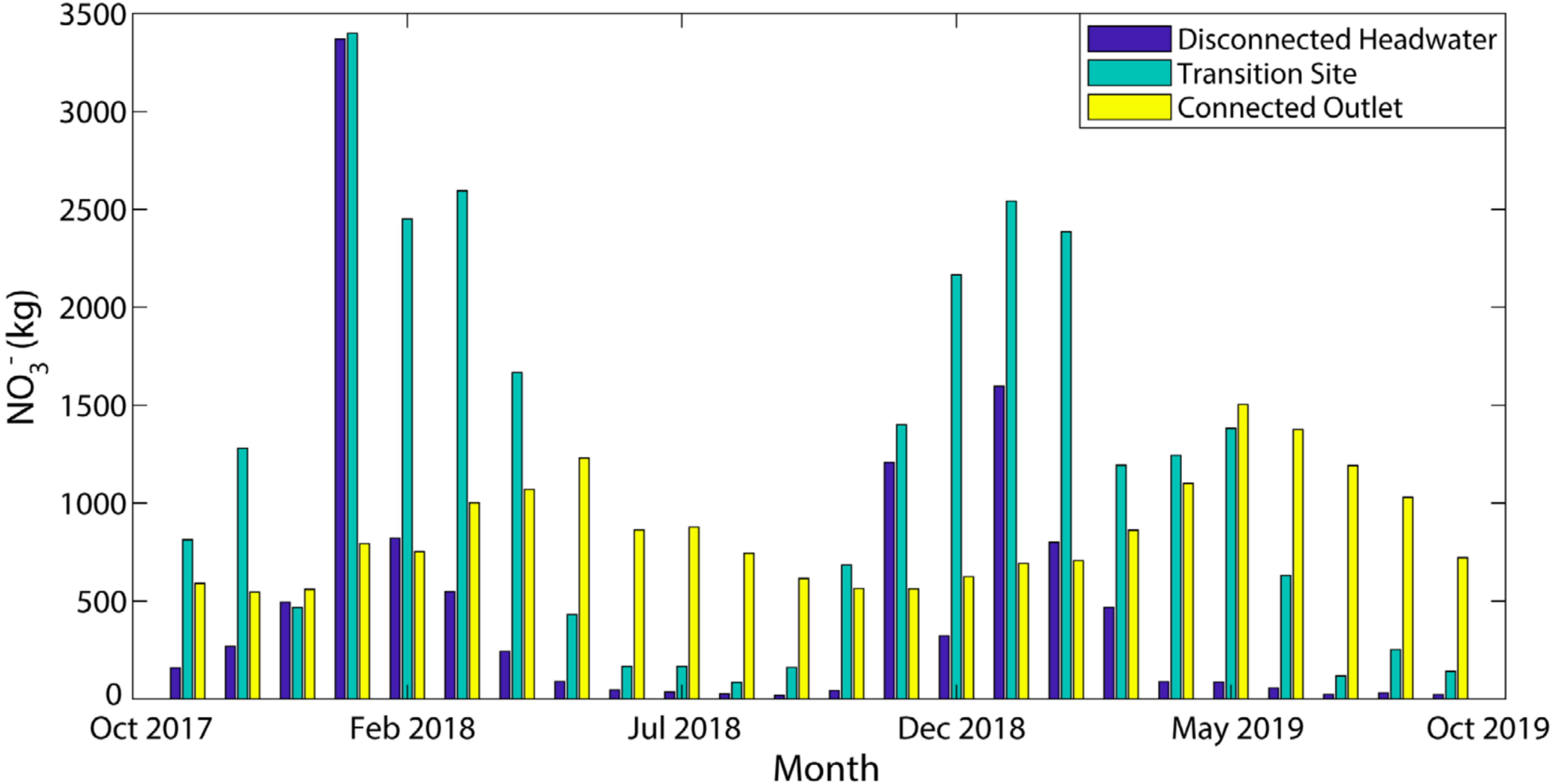


Default Excel graph (yikes!)

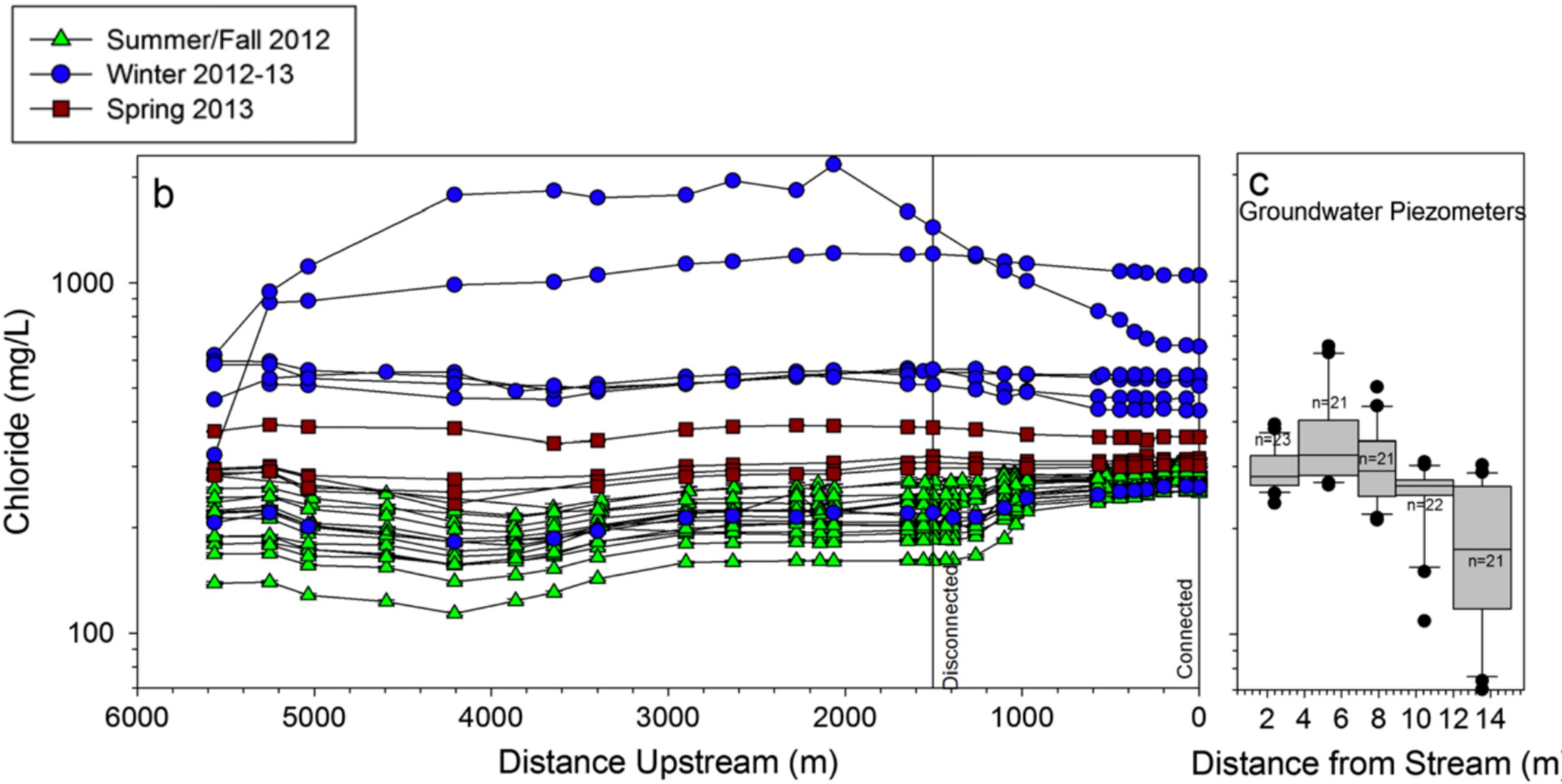


A few ways to plot water chemistry data:

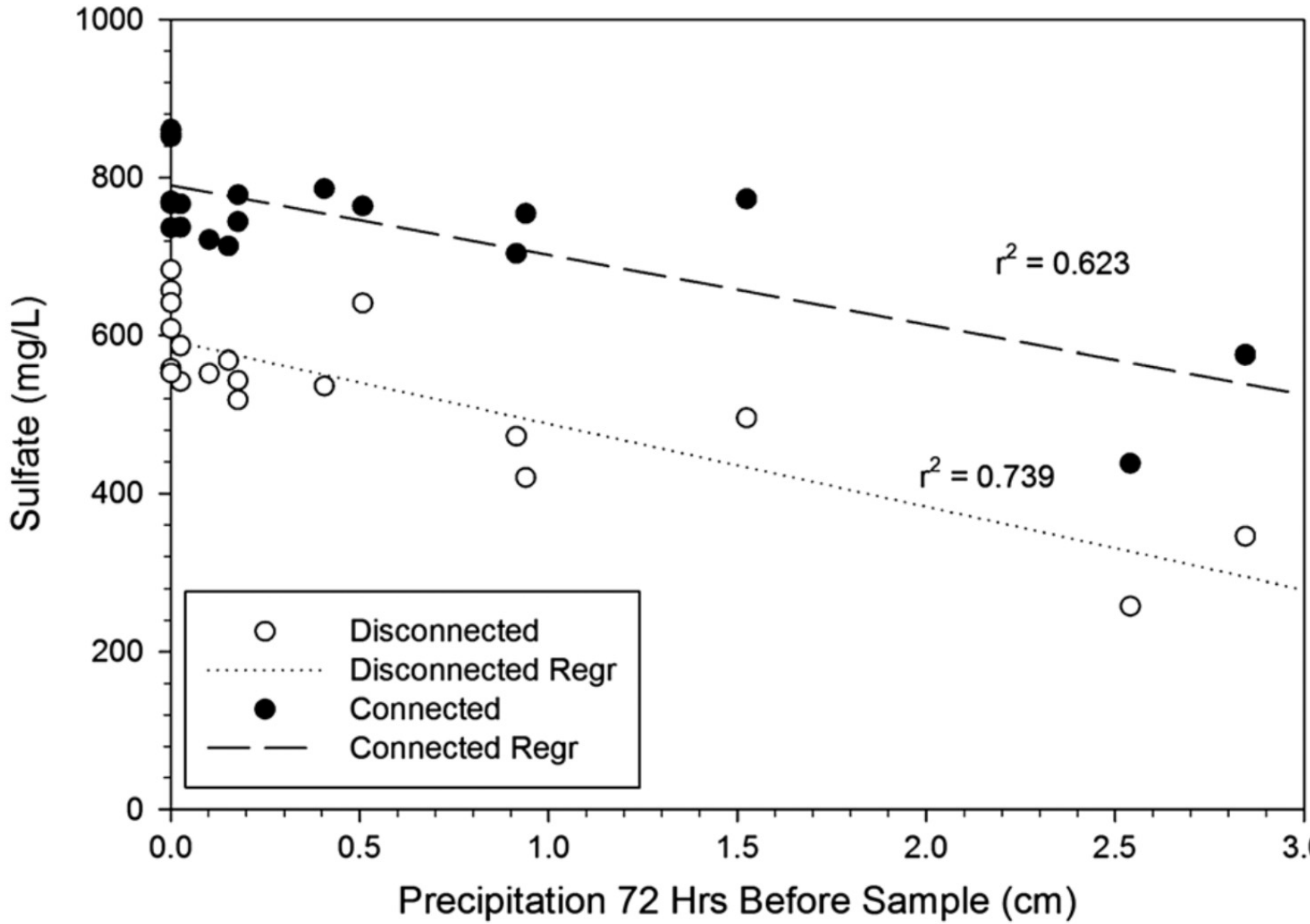
- Measured value (e.g., concentration, conductivity, temperature, pH) as a function of a variable (distance, depth, time)
- Measured value A vs measured value B
- Solute ratios (to account for changes in concentration due to water volume or to compare different sources)
  - Cl is often considered to be *conservative* (does not chemically react, derives mostly from precipitation) and is used to normalize data to account for changes in water volume due to evapotranspiration or dilution
- Ternary or Piper diagrams – summaries chemical composition of water samples; classifies water on the basis of relative proportions of major ions



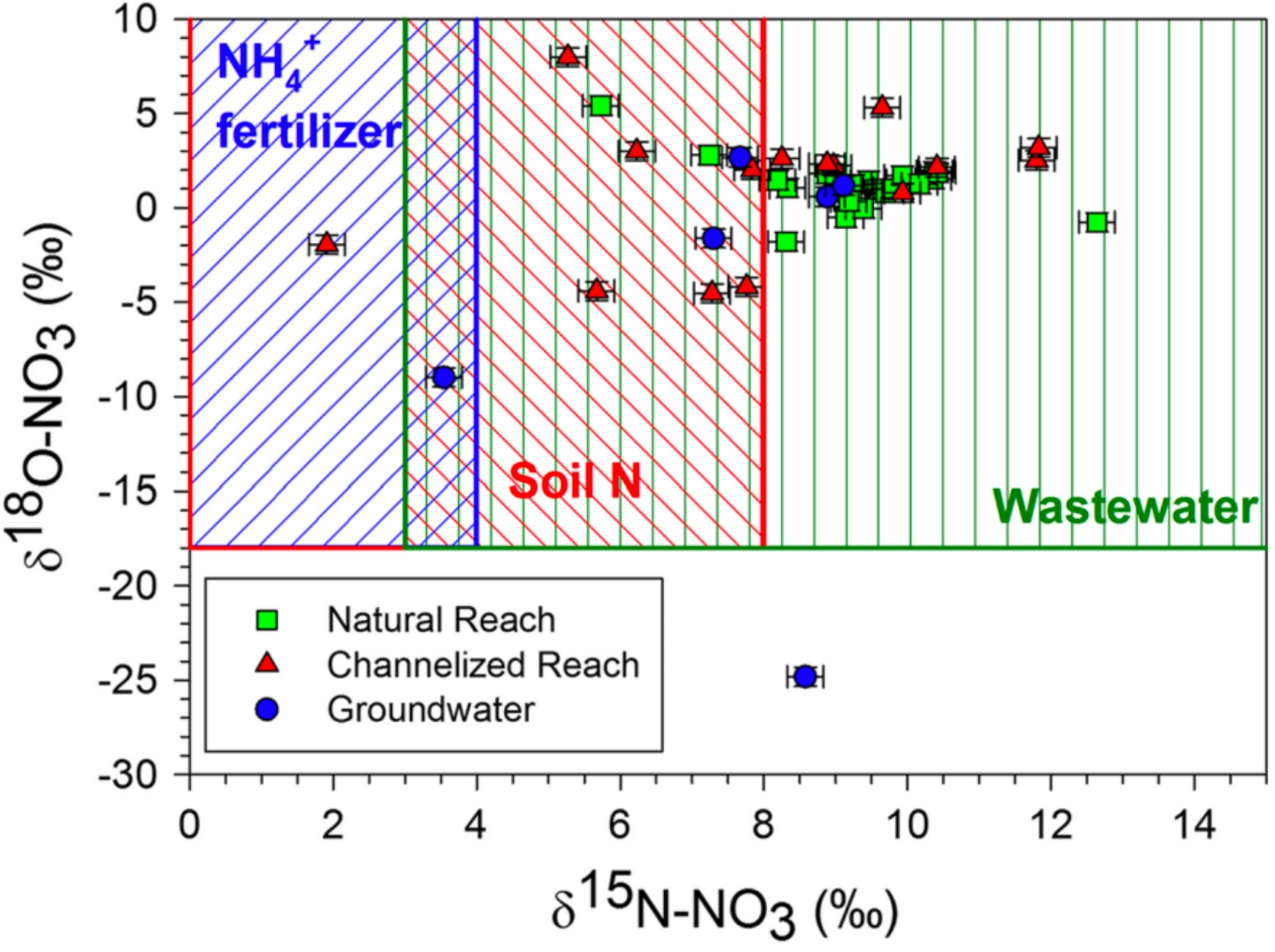
Disconnected Headwater
Transition Site
Connected Outlet
3500
3000
2500
2000
1500
1000
500
0
NO_3^- (kg)
Oct 2017
Feb 2018
Jul 2018
Dec 2018
May 2019
Oct 2019
Month



Summer/Fall 2012
Winter 2012-13
Spring 2013
b
Chloride (mg/L)
1000
100
Disconnected
Connected
6000
5000
4000
3000
2000
1000
0
Distance Upstream (m)
c
Groundwater Piezometers
n=23
n=21
n=21
n=22
n=21
2
4
6
8
10
12
14
Distance from Stream (m)

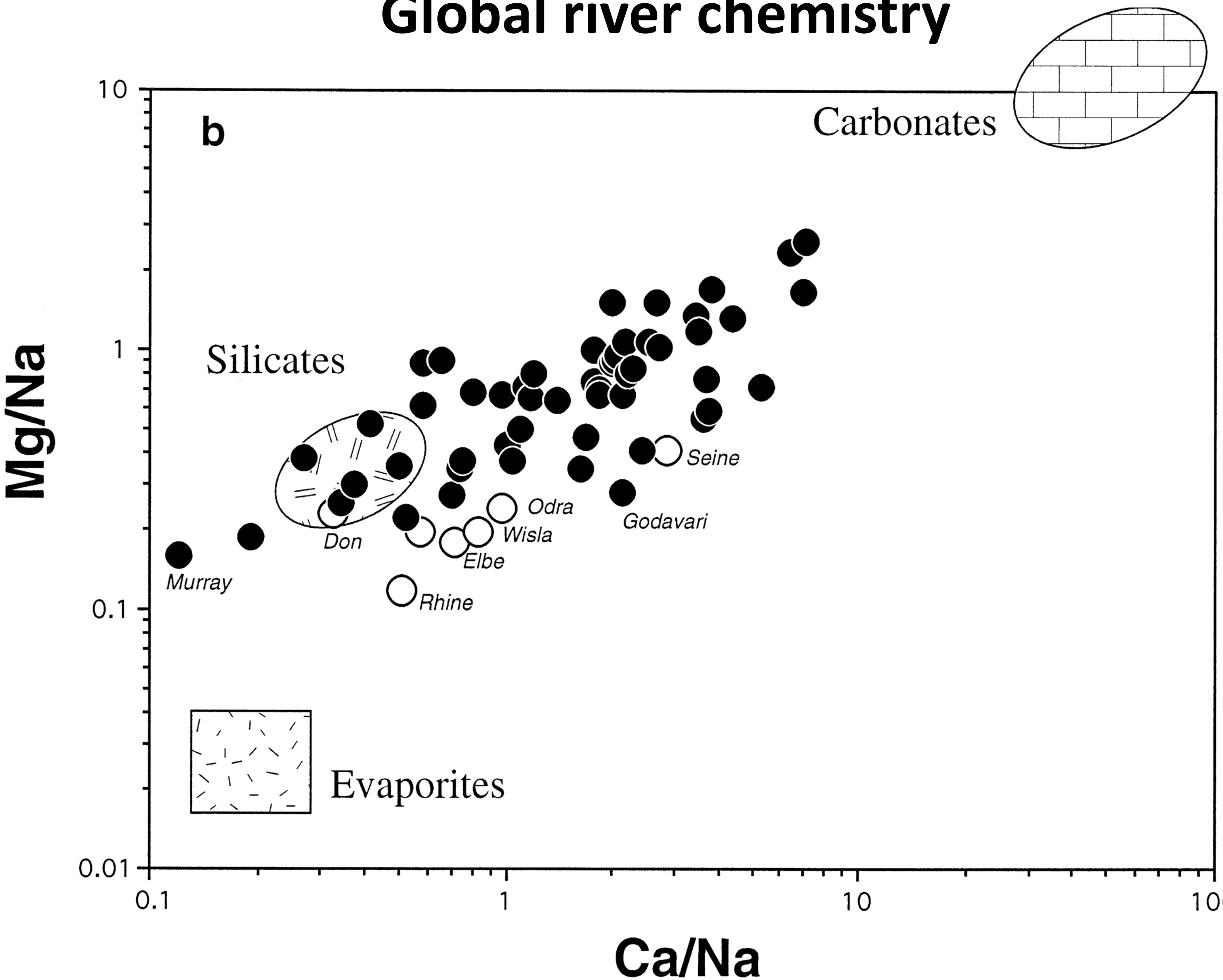


Sulfate (mg/L)
1000
800
600
400
200
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Precipitation 72 Hrs Before Sample (cm)
$r^2 = 0.623$
$r^2 = 0.739$
Disconnected
Disconnected Regr
Connected
Connected Regr



NH$_4^+$
fertilizer
Soil N
Wastewater
Natural Reach
Channelized Reach
Groundwater
δ^{18}O-NO$_3$ (‰)
δ^{15}N-NO$_3$ (‰)
10
5
0
-5
-10
-15
-20
-25
-30
0
2
4
6
8
10
12
14

Global river chemistry

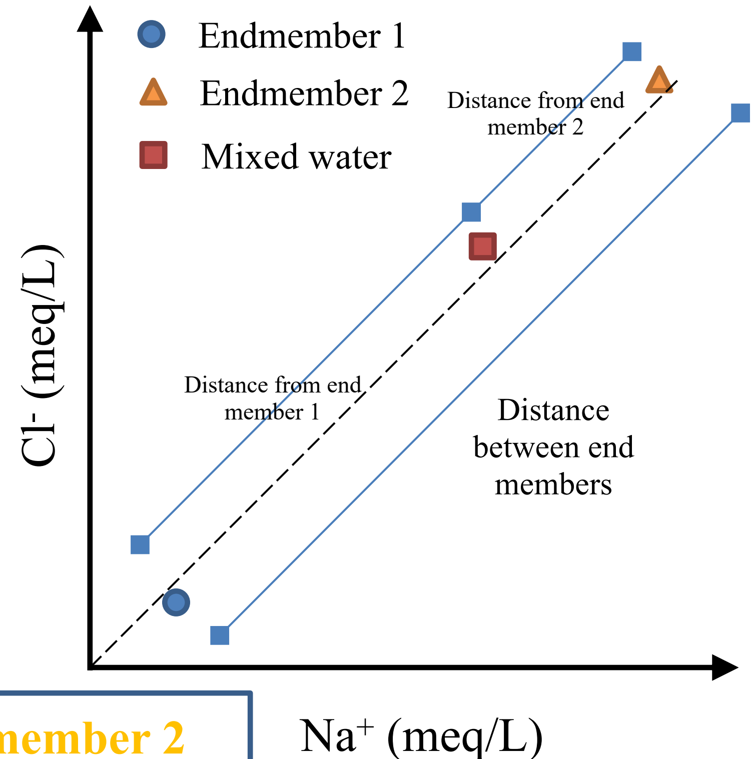


Gaillardet et al., 1999

Bivariate Plot
End Member Mixing

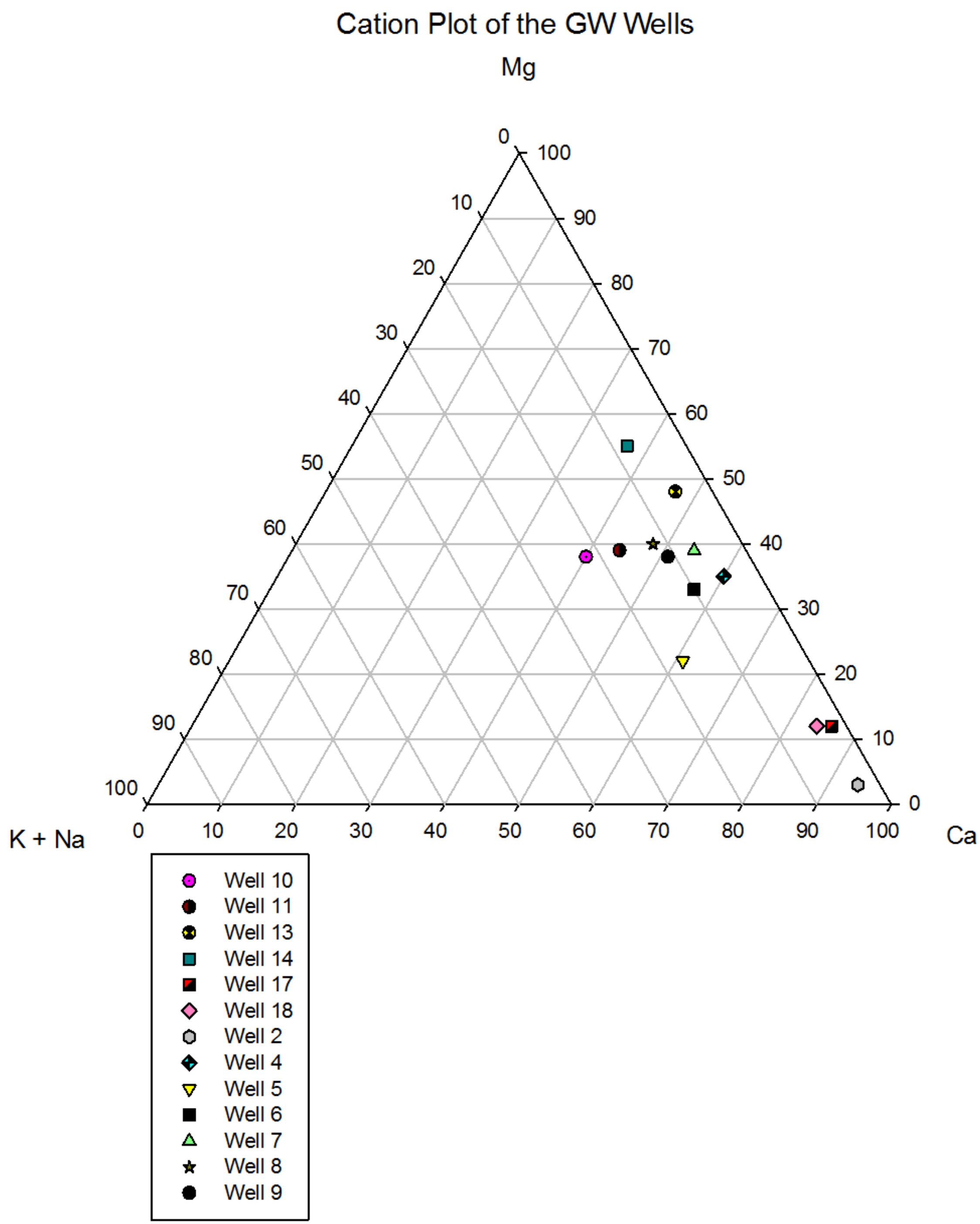
To compute the percent mixing in a sample, you can simply measure distances on the bivariate plots (e.g. Cl vs Na).

Simply measure (with i.e. with a ruler) distances off of a graph.



Percent of **endmember 1** in the mixed water = Distance from **endmember 2** / Distance between endmembers

Percent of **endmember 2** in the mixed water = Distance from **endmember 1** / Distance between endmembers

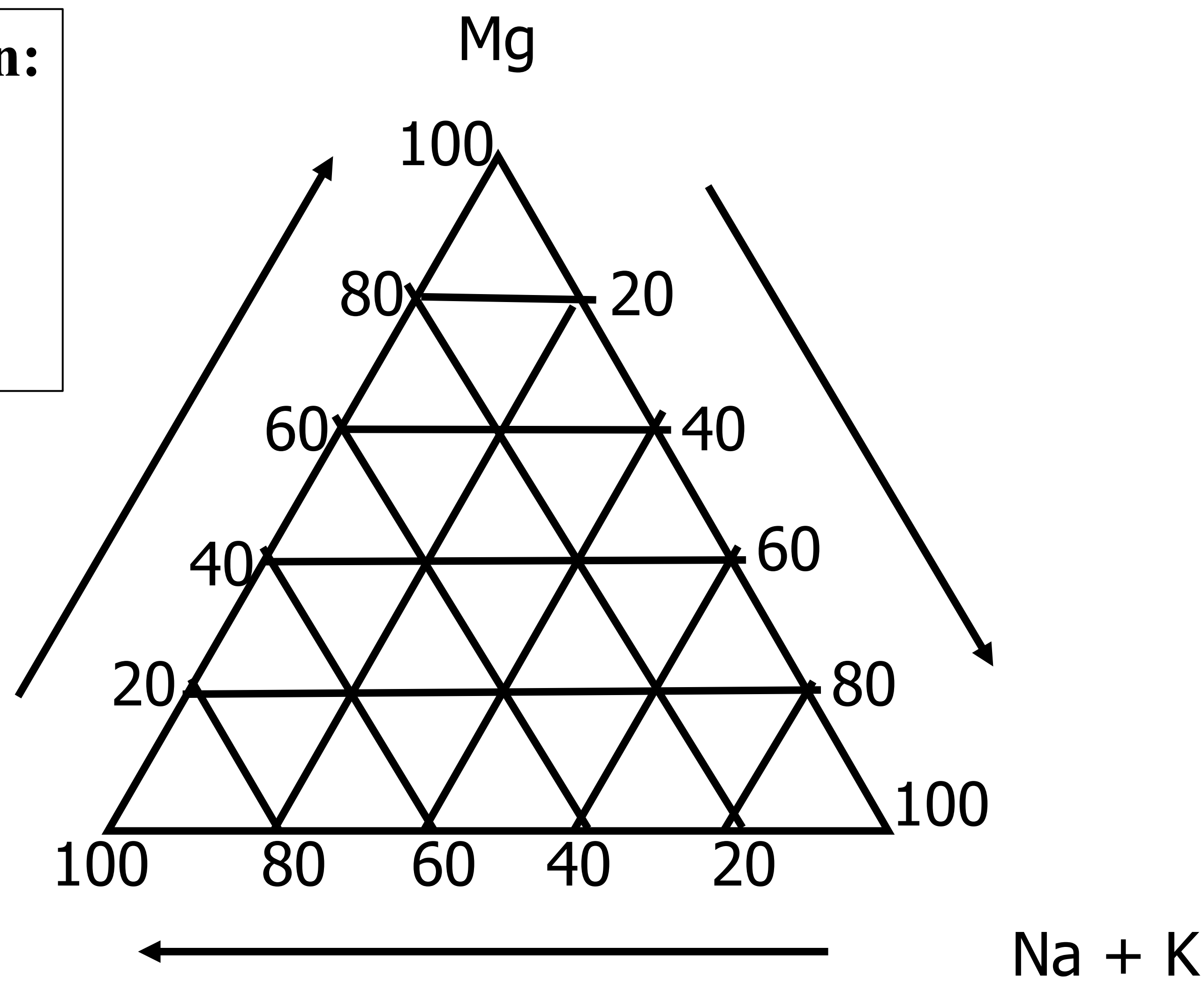

Cation Plot of the GW Wells
Mg
K + Na
Ca
0
10
20
30
40
50
60
70
80
90
100
Well 10
Well 11
Well 13
Well 14
Well 17
Well 18
Well 2
Well 4
Well 5
Well 6
Well 7
Well 8
Well 9

Piper Plot

- Combination of two tri-linear plots
  - One tri-linear plot of anions (Cl, SO_4, HCO_3)
  - One tri-linear plot of cations (Ca, Mg, Na+K)
- Concentrations are plotted as a percentage of the total concentrations in the unit of meq/L for cations (or anions)
  - i.e., 50% Ca, 40% Mg, 10% Na+K
- Locations on triangles are projected onto a diamond – point is plotted where they meet
- Sometimes the circle shows the relative total ion concentrations (TDS)

Example of Tri-linear Plot

For a water solution:
48 mg/L Mg
11.5 mg/L Na
19.5 mg/L K
100 mg/L Ca



Example of Tri-linear Plot

Using the formula masses:
Na = 23.0g
Ca = 40.0g
Mg = 24.0g
K = 39.0g

For a water solution:
48 mg/L Mg^{2+}
11.5 mg/L Na^{+}
19.5 mg/L K+
100 mg/L Ca^{2+}

2 mmol/L Mg
0.5 mmol/L Na
0.5 mmol/L K
} 1 mmol/L Na+K
2.5 mmol/L Ca

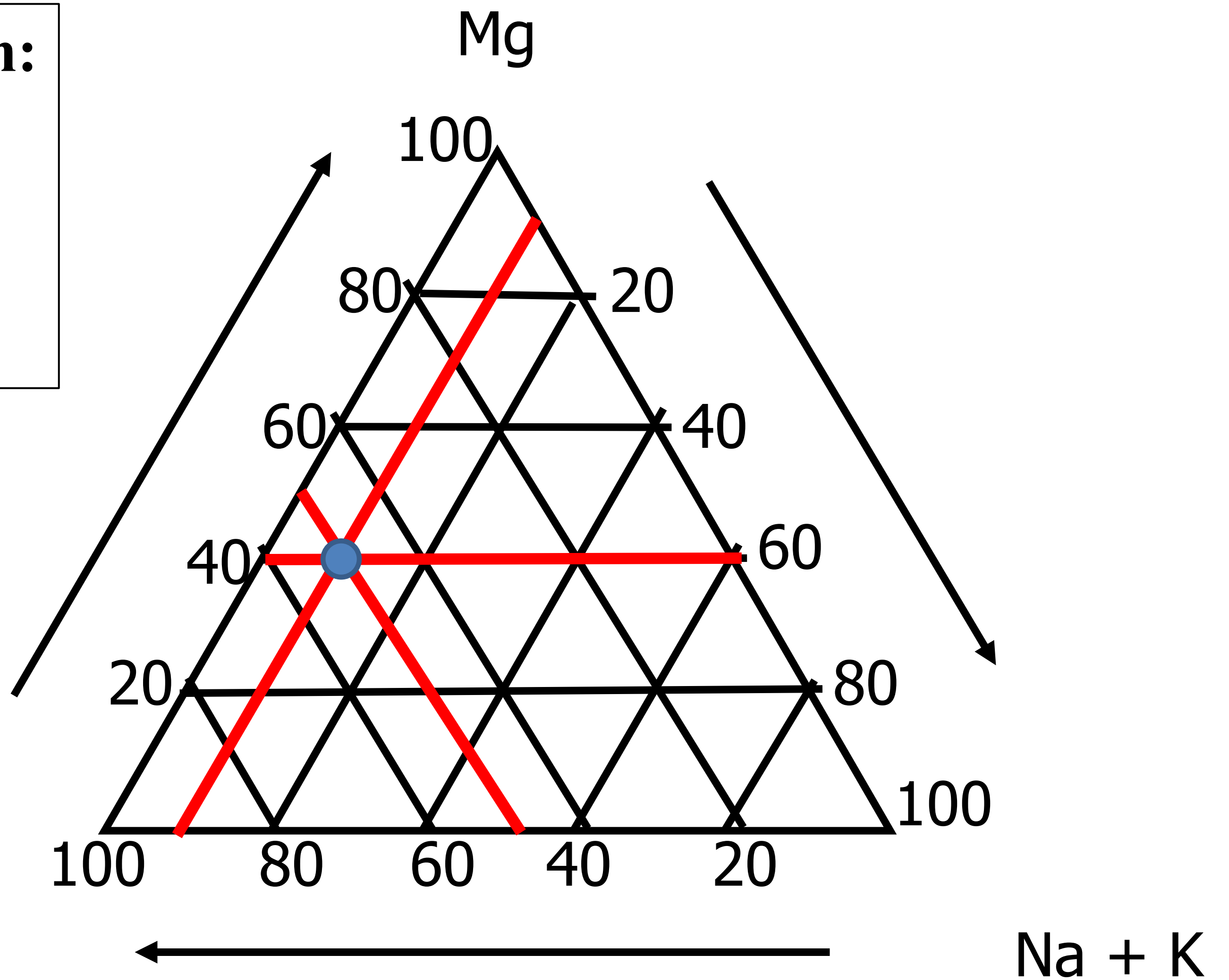
4 meq/L Mg
1 meq/L Na+K
5 meq/L Ca

40% Mg
10% Na+K
50% Ca

Example of Tri-linear Plot

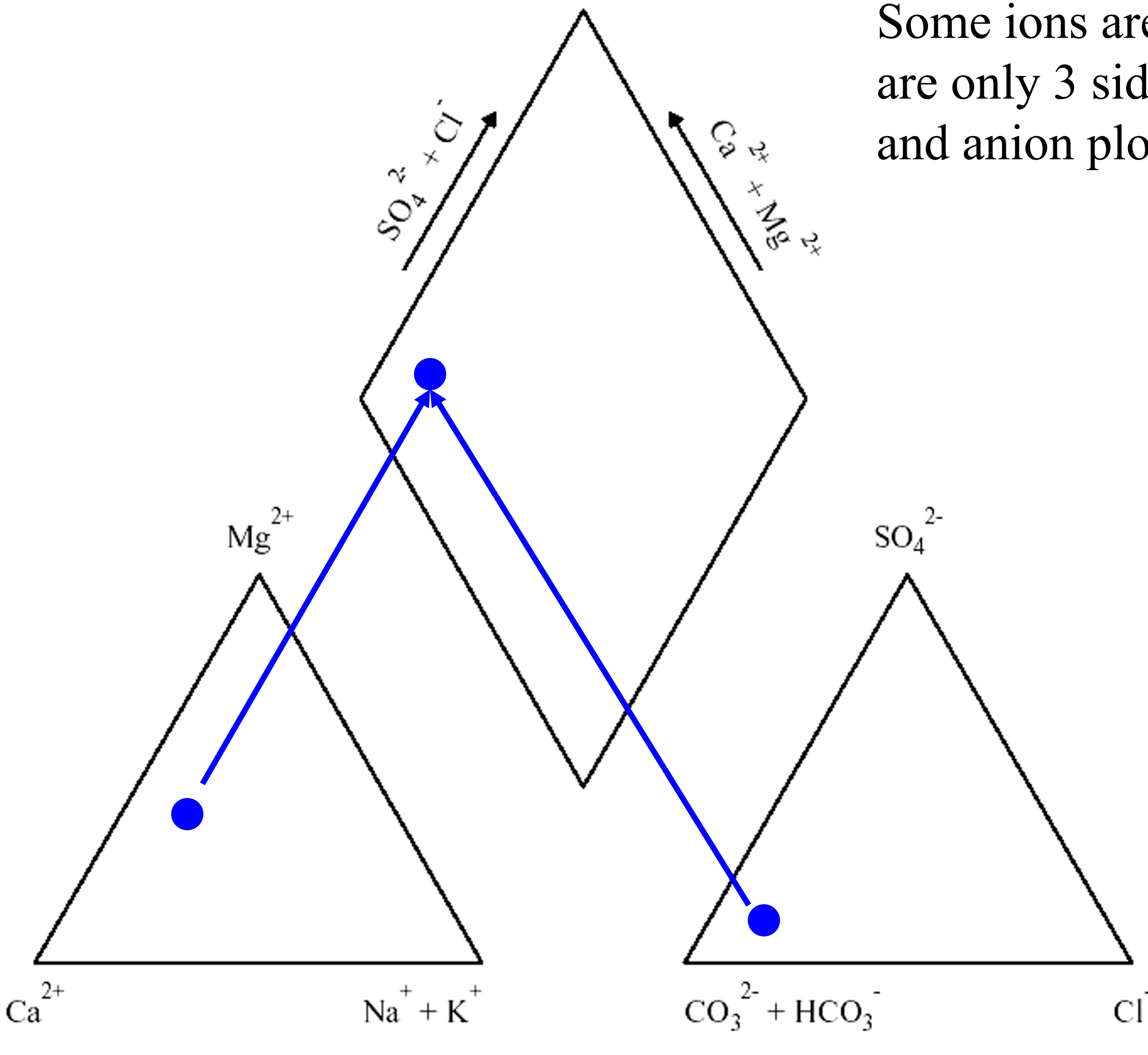
For a water solution:
48 mg/L Mg
11.5 mg/L Na
19.5 mg/L K
100 mg/L Ca

40% Mg
10% Na+K
50% Ca



Piper Plots

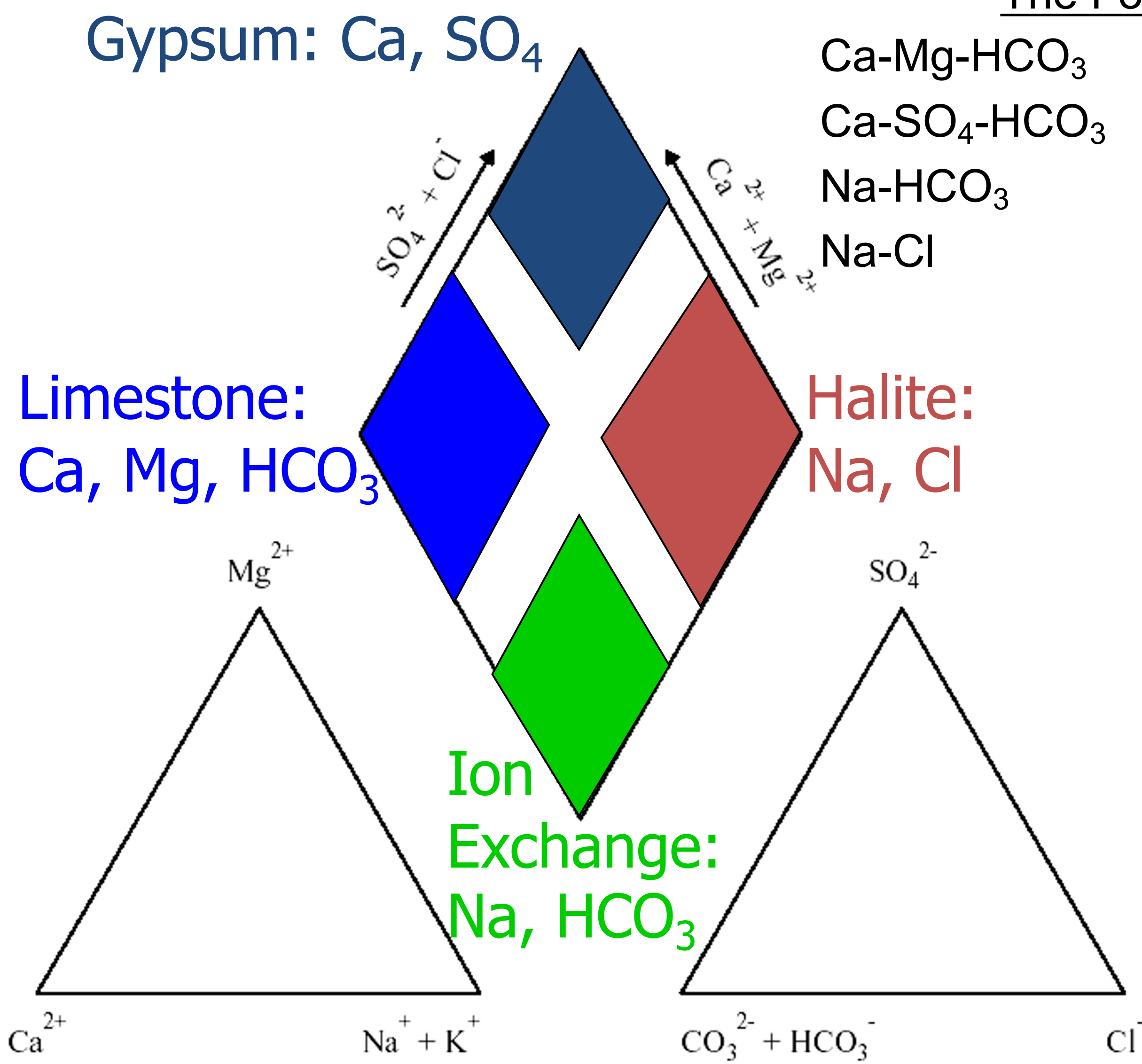
Some ions are added as there are only 3 sides on the cation and anion plots



Geochemical Facies

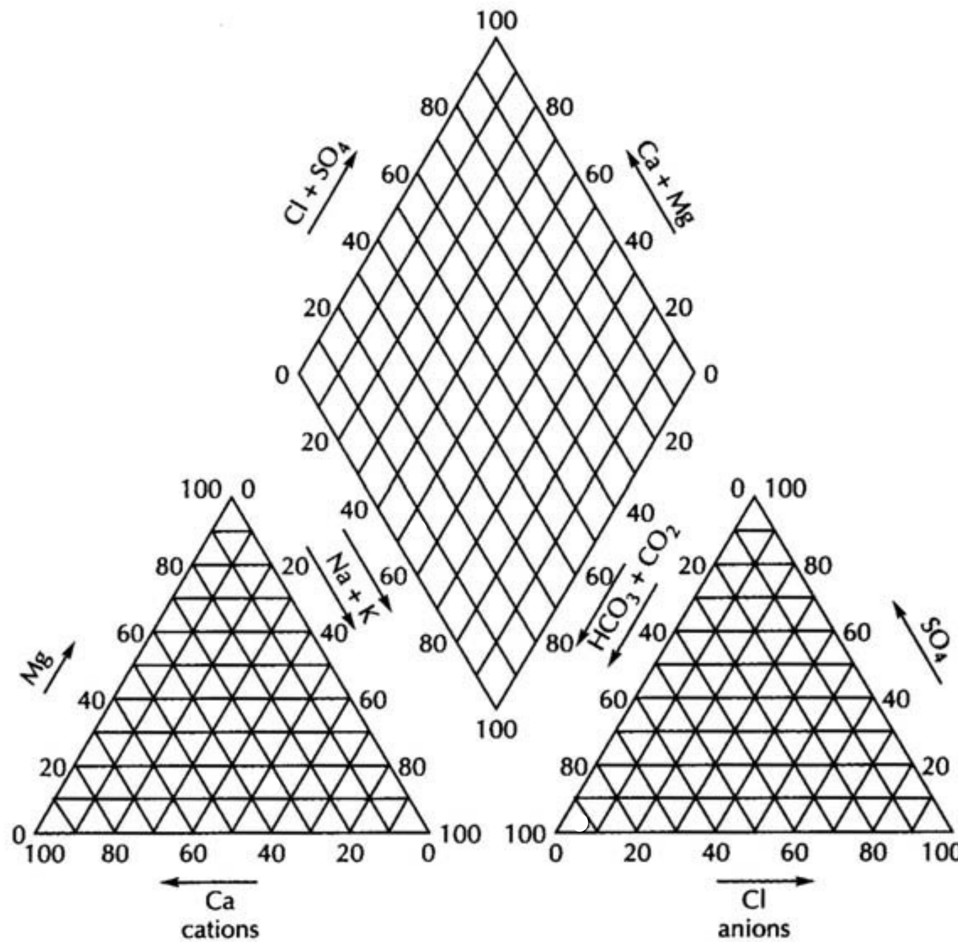
<u>The Four Major Water Types:</u>

Ca-Mg-HCO_3	Associated w/ limestone
Ca-SO_4-HCO_3	Associated w/ gypsum
Na-HCO_3	Associated w/ ion-exchange
Na-Cl	Associated w/ halite/brines



Summary – Piper Plot

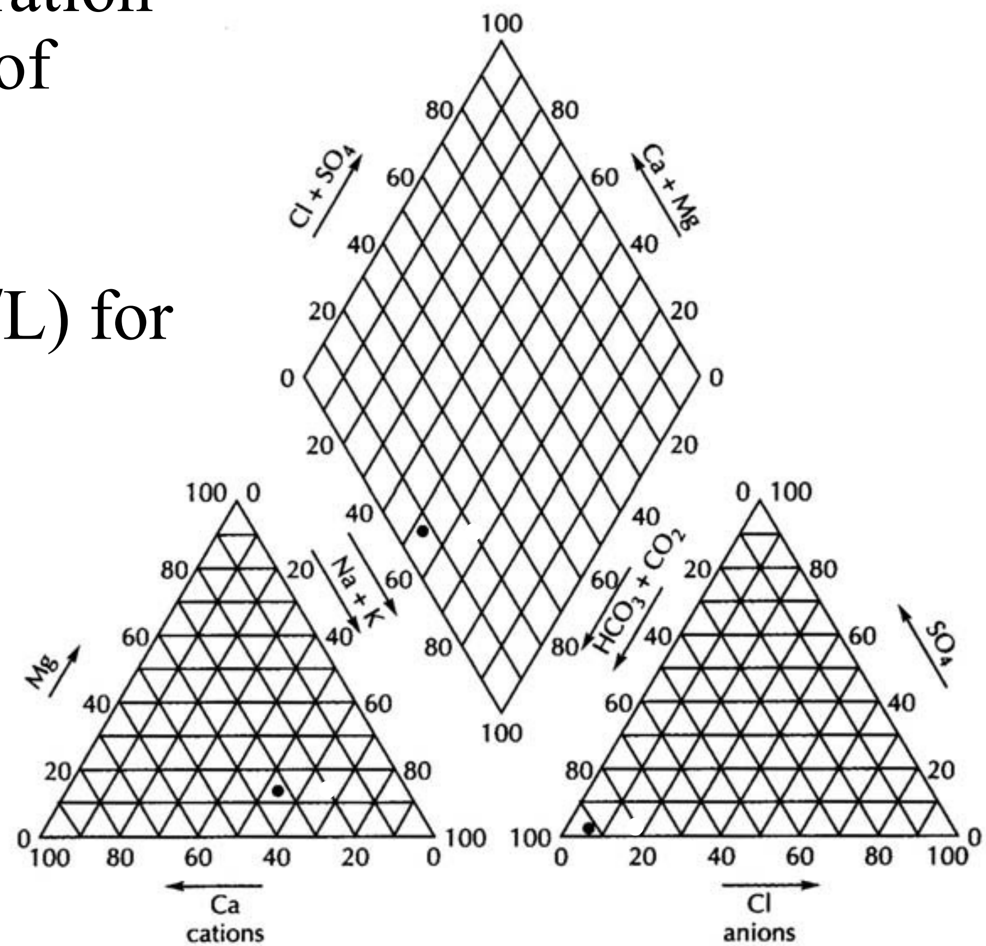
1. Measure the concentrations of the major ions:
   - Mg^{2+}
   - Ca^{2+}
   - Na^{+} and K^{+}
   - SO_4^{-}
   - Cl^{-}
   - $HCO_3^{-} + CO_2$



Summary – Piper Plot

2. Calculate the concentration of each ion (or group of ions) in meq/L
3. Calculate the relative concentration (%meq/L) for cations and anions
4. Plot results.

- On each axis is the %meq/L of each ion (or combination of ions)



Practice Example for Piper Plot

Table 10.3 Inorganic Chemistry of Typical Natural Water Samples (mg/L)

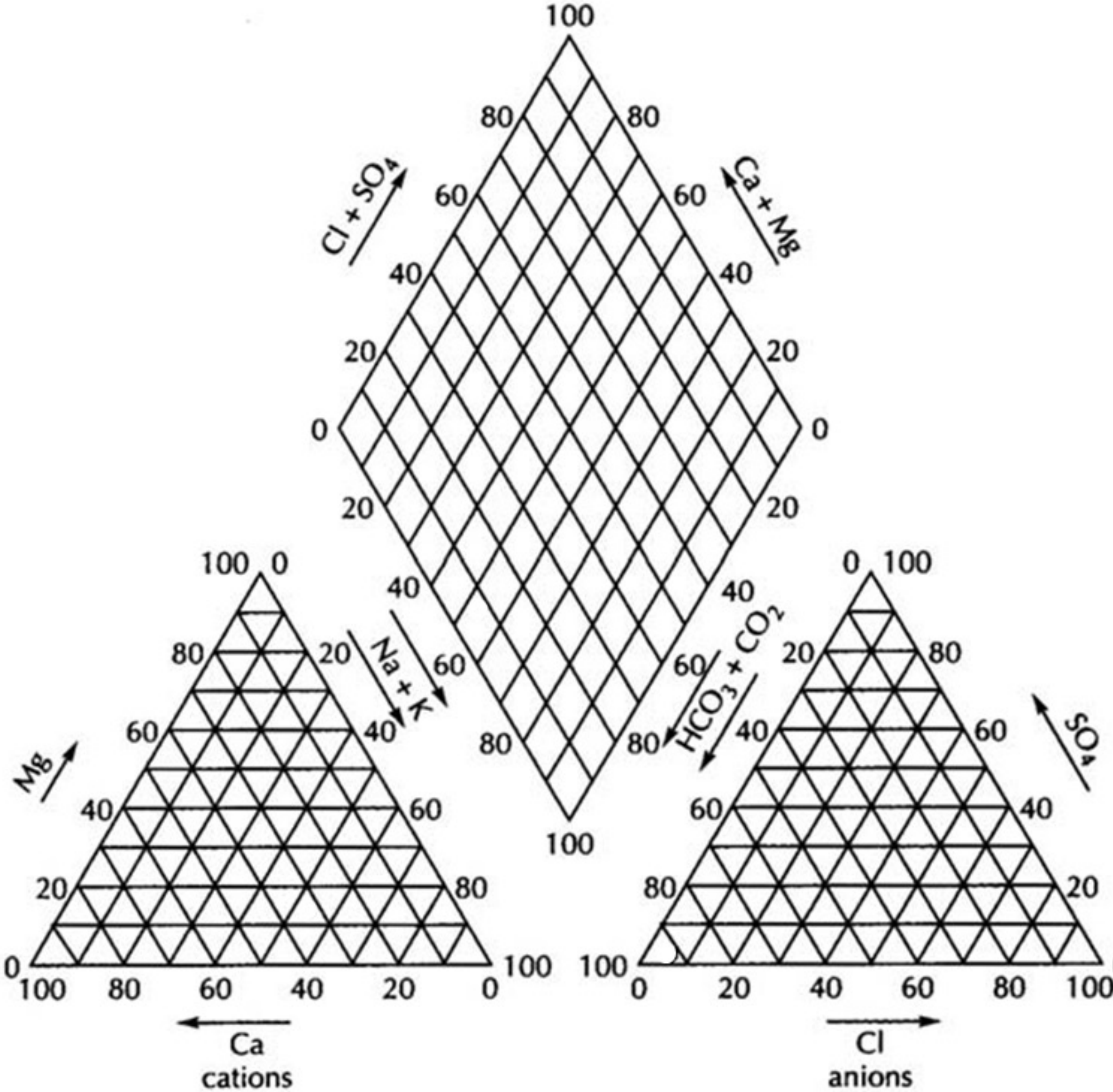
Source	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	SiO_2^*	TDS
Precipitation:										
1	4.3	0.26	0.03	0.07	0.05	—	3.03	0.24	—	6
2	5.4	0.41	0.59	4.36	0.10	—	1.97	8.2	—	16
Sea Surface:										
3	7.8	423	1320	11,100	410	129	2790	19,900	1-10	36,100
Rivers:										
4	—	19	2.3	6.4	1.1	68	7.0	6.5	11.1	122
5	—	83	24	95	5.0	135	270	82	9.3	703
Groundwater:										
6	6.9	10	1.5	5.0	0.8	19	5.5	11	—	49
7	7.6	24.5	10.7	24.9	4.7	170	21.8	7.1	56.5	234
8	7.5	69	29	3.5	1.1	297	37	9.4	11	320
9	6.9	21	3.1	170	8.4	400	12	85	12	510
10	7.3	210	100	2000	46	300	1200	3000	6.7	6700

From Fitts Table 10.3

%meq/L (some rounding errors)

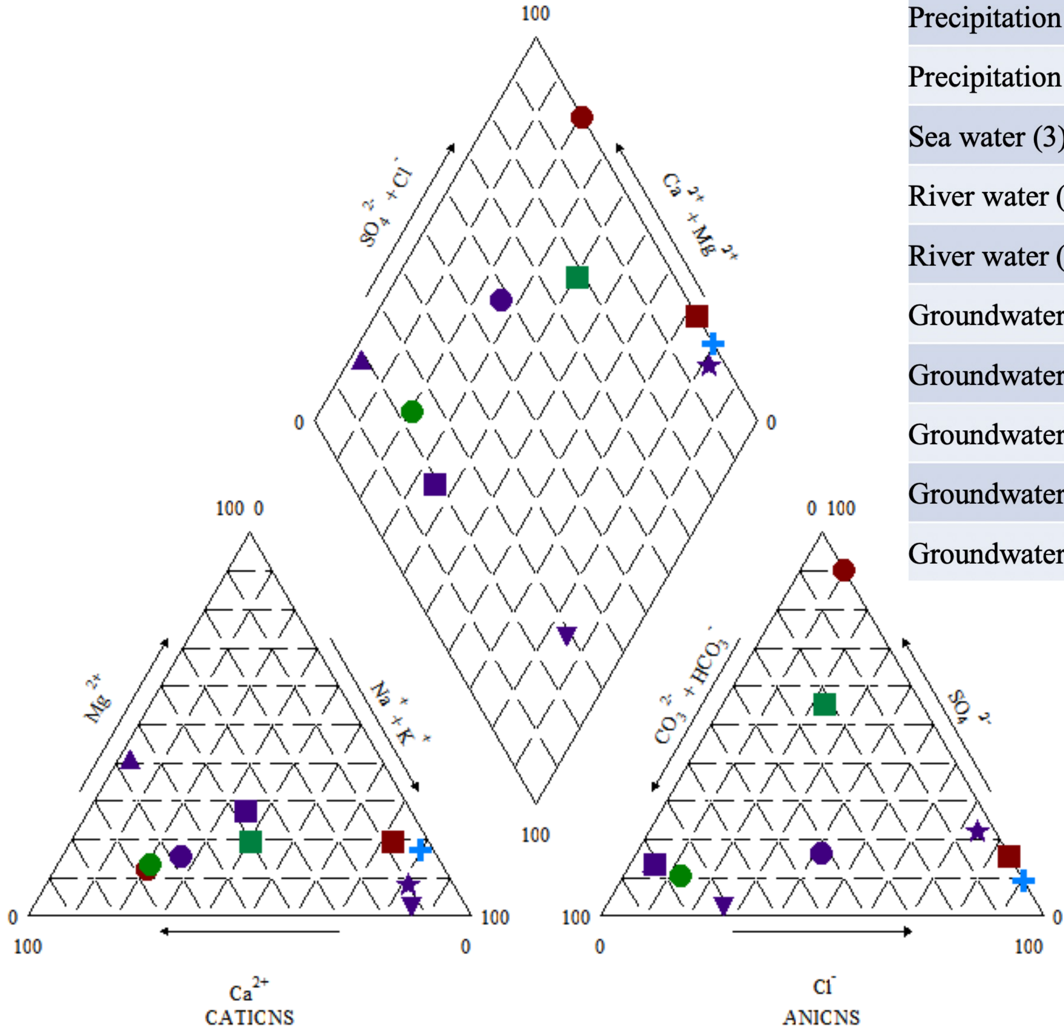
Source	Cations (+) Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	$Na^{+} + K^{+}$	Anions (-) HCO_3^{-}	SO_4^{2-}	Cl^{-}
Precipitation (1)	67	12	15	6	21	0	90	10
Precipitation (2)	8	19	72	1	73	0	15	85
Sea water (3)	3	17	78	2	80	0	9	91
River water (4)	66	13	19	2	21	77	10	13
River water (5)	40	19	40	1	41	22	55	23
Groundwater (6)	59	14	25	2	27	42	16	42
Groundwater (7)	36	27	33	4	37	81	13	6
Groundwater (8)	57	40	3	0	3	83	13	4
Groundwater (9)	12	3	83	2	85	71	3	26
Groundwater (10)	10	8	81	1	82	4	22	74

Practice Example for Piper Plot



Solution

Source	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	$Na^{+} + K^{+}$	HCO_3^-	SO_4^{2-}	Cl^-
Precipitation (1)	67	12	15	6	21	0	90	10
Precipitation (2)	8	19	72	1	73	0	15	85
Sea water (3)	3	17	78	2	80	0	9	91
River water (4)	66	13	19	2	21	77	10	13
River water (5)	40	19	40	1	41	22	55	23
Groundwater (6)	59	14	25	2	27	42	16	42
Groundwater (7)	36	27	33	4	37	81	13	6
Groundwater (8)	57	40	3	0	3	83	13	4
Groundwater (9)	12	3	83	2	85	71	3	26
Groundwater (10)	10	8	81	1	82	4	22	74



Blue = seawater
Green = river water
Brown = precipitation
Purple = GW

purple square = 5
purple triangle = 8
purple star = 10

Data Objectives:

1. Construct calibration curves
2. Calculate linear regression statistics, including analytical error
3. Convert raw data to concentrations
4. Plot water chemistry to highlight similarities and differences between water sources