Water Chemistry 4

Use of Chemical Analyses to Interpret Ground Water Systems

When groundwater flows through rocks their minerals dissolve gradually rarely reaching their solubility limit

So their CONCENTRATION in a groundwater gample generally reflects RESIDENCE TIME of water in the subsuface

DISSOLVED CONSTITUENTS REFLECT:

- **type of rocks water flowed through**
- **impacts of man**
- **character of the constituent & condition of the water**

Let's look at sources and impacts of a few common constituents

Calcium (Ca^{2+})

- **Most abundant of the alkaline-earth metals**

Z	Element	No. of electrons/shell
4	Beryllium	2, 2
12	Magnesium	2, 8, 2
20	Calcium	2, 8, 8, 2
38	Strontium	2, 8, 18, 8, 2
56	Barium	2, 8, 18, 18, 8, 2
88	Radium	2, 8, 18, 32, 18, 8, 2

- **Derived from nearly all rocks**
  (sedimentary, igneous, metamorphic)
- **Mostly from**
  calcite ($CaCO_3$) and gypsum ($CaSO_4$-$2H_2O$) which are common in sedimentary rocks (limestone is ~10% of sed. rocks)
- **Contributes to hardness which inhibits lathering**

Magnesium (Mg^{2+})

- In many minerals, e.g. dolomite ($CaMg(CO_3)_2$) magnesite ($MgCO_3$) and clays
- Sometimes introduce to water from mining
- Occurs in underground reservoirs of brine

Sea Water Ion Percentage (by mass)

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 which inhibits lathering

Sodium (Na+)

- In feldspars, evaporates, and clays
- Second most abundant element dissolved in seawater

Sea Water Ion Percentage (by mass)

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 %

- Mobile often indicates human impact:
  e.g. road de-icing, water softeners, human or animal waste disposal, leachate from landfills
- Often associated with chloride and bromide

Potassium (K^+)

- In potassium feldspars and micas
- An important fertilizer component - its presence is of great importance for soil health, plant growth and animal nutrition
- Often associated with chloride and bromide

Boron (B)

- In rocks, but natural background concentrations are low (typically < 10 μg/L to 40 μg/L)
- Humans introduce boron by using non-chlorine bleach, making fiberglass, combusting coal, melting copper, and applying fertilizers
- Boron does not undergo biological removal during treatment and is not significantly sorbed in the subsurface so it is mobile and thus a good indicator of sewage systems effecting groundwater

Sulfate (SO_4^{-2})

- **Gypsum** ($CaSO_4$-$2H_2O$) most important natural source
- Humans introduce sulfate by **atmospheric deposition from burning fossil fuels, fertilizer use, and land application of animal waste**, and
- **acid mine drainage** because exposure of pyrite to oxygen and water produces sulfuric acid

Phosphates (PO_4^{-3})

- Phosphorus is usually present as phosphate
- Sources:
  - **wastewater and septic systems** organic phosphates in body waste & food residues
  - **animal waste**
  - **detergents & fertilizers**
  - **industrial discharge** phosphates are added to water to prevent formation of iron oxides or calcium carbonates
  - **development/paved surfaces** because soil erosion releases phosphorus
  - **forest fires** due to soil erosion

Nitrate (NO_3^-)

- Enters water through the nitrogen cycle rather than via dissolving minerals
- Human sources: septic systems, feed lots, and fertilizers
- Under aerobic conditions, NO_3^- is stable and tends to be conservative in most groundwater environments (no water-rock interaction … not sorbed to soil/rock)

Bromide (Br^-)

- From sea water Br^- ~65 mg/l (~0.2% of ions by mass)
- Br is conservative so Br/Cl ratio is used to trace origins of salinity (ocean water Br/Cl = 0.0035)
  e.g.
  - groundwater in rock with Halite dissovles NaCl so Br/Cl decreases as Cl increases
  - evaporation to the point where Halite precipitates decreases Cl so Br/Cl increases
- > 0.05 mg/l Br in fresh water may indicate pesticides or biocides
  - Bromine disinfects swimming pools & cooling towers
  - Organic bromines are used as sprays to kill pests

Chloride (Cl^-)

- Chlorine as Cl_2 is highly toxic, it is used in disinfectants, paper production (bleach), antiseptics, dyes, insecticides, paints, petroleum products, plastics, solvents
- Chloride (Cl^-) is a salt resulting from combining chlorine gas and a metal (NaCl, $MgCl_2$) most are highly soluble in water
- Sources: rocks containing chlorides, agricultural runoff, wastewater from industries, oil well wastes, wastewater treatment plant effluent, deicing roads
- Conservative so used in mass balance calculations for mixing of water bodies

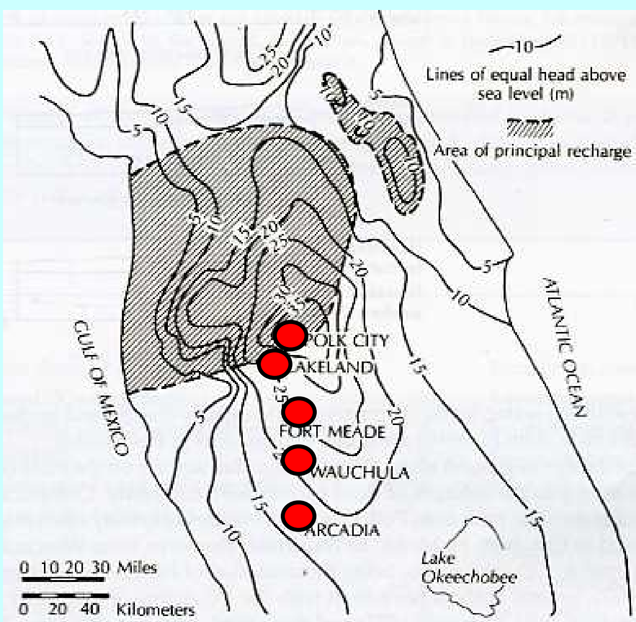
Chloride (Cl^-)

Water samples are collected from a well in the park, the river, and wells in the local aquifer. Based on the water chemistry, the park water was a mixture of aquifer and river water. What is the mixing ratio?

	Cl (mg/L)
Park	32
River	15
Local Aquifer	39

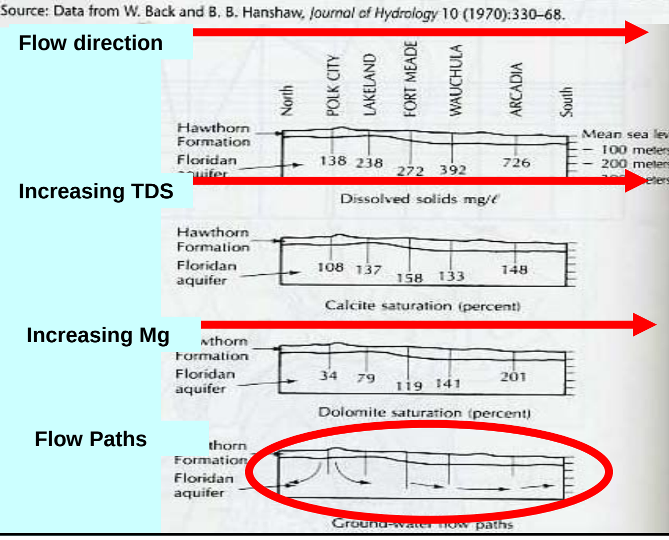
Next we look at a few groundwater systems to see how groundwater chemistry relates to flow and geology

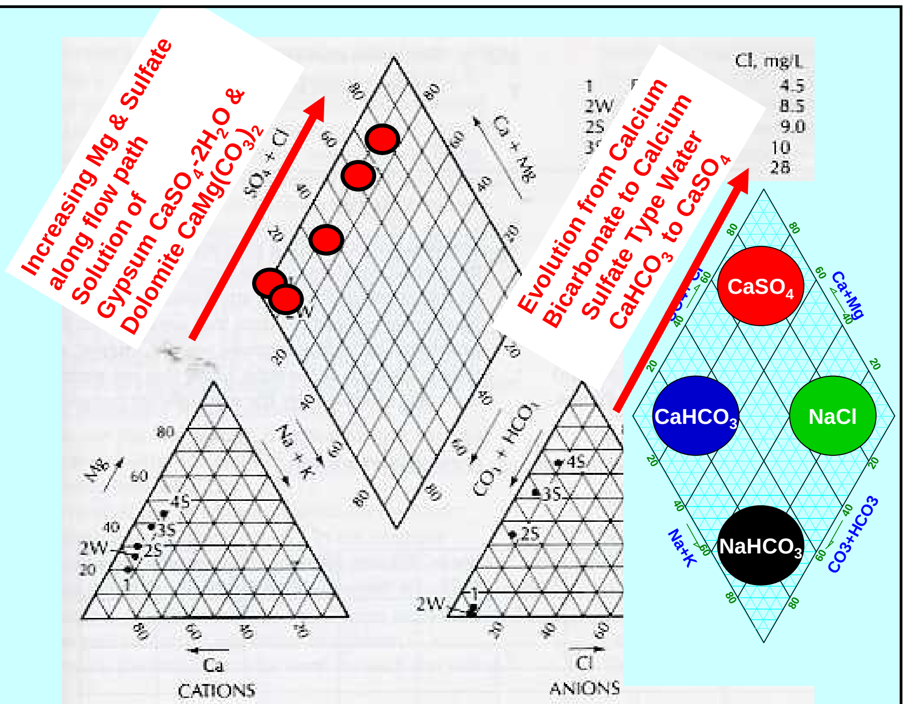
Floridan Aquifer (limestone)
Potentiometric surface



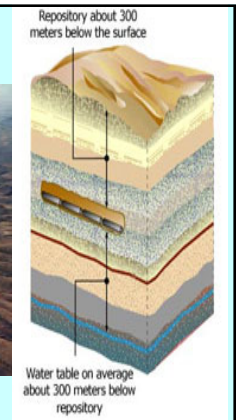
Well	Location	Temp % C	Field pH	SiO_2	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	CL^-	TDS
				Milligrams per liter								
1	Polk City	23.8	8.0	12	34	5.6	3.2	0.5	124	2.4	4.5	138
2W	Lakeland	26.3	7.62	18	54	14	6.9	1.0	253	3.6	8.5	238
2S	Ft. Meade	26.6	7.75	16	58	17	6.1	0.7	163	71	9.0	272
3S	Wauchula	25.4	7.69	18	66	29	8.3	2.0	168	155	10	392
4S	Arcadia	26.3	7.44	31	106	60	21	3.7	206	344	28	726

Source: Data from W. Back and B. B. Hanshaw, *Journal of Hydrology* 10 (1970):330–68.





Death Valley Springs



- **Yucca Mountain is a test site for a high-level nuclear waste repository**
- **Advantages: arid, geologically stable, remote, deep water table, closed water basin**
- **The repository is in the unsaturated zone ~1000ft below surface & ~1000ft above water table**
- **At depth is an extensive, highly permeable Carbonate Aquifer**

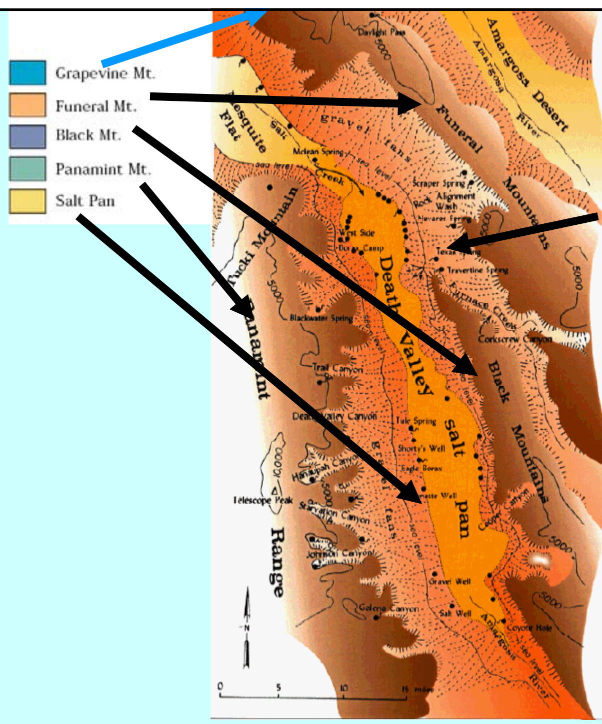
Research suggests Yucca Mountain groundwater is hydraulically connected to the Regional Lower Carbonate Aquifer and Death Valley is believed to be a discharge point for regional ground water below Yucca Mountain

Discharge from the major springs in Death Valley may be fault-controlled, but the geology is complex, surface geology is known, but few boreholes penetrate beneath the thick alluvium

Thus a Geochemical study of spring waters was done in an effort to determine the source of springs in Death Valley

Death Valley National Park 289 Mapped Springs

Spring fed Salt Creek hosts a unique suite of pupfish comparable to the presence of land tortoises and Darwin's finches on the Galapagos Islands



Nevares

Texas

Travertine

Largest combined discharge ~2500 GPM

From Paleozoic Carbonates Same age as Lower Carbonates below Yucca Mtn

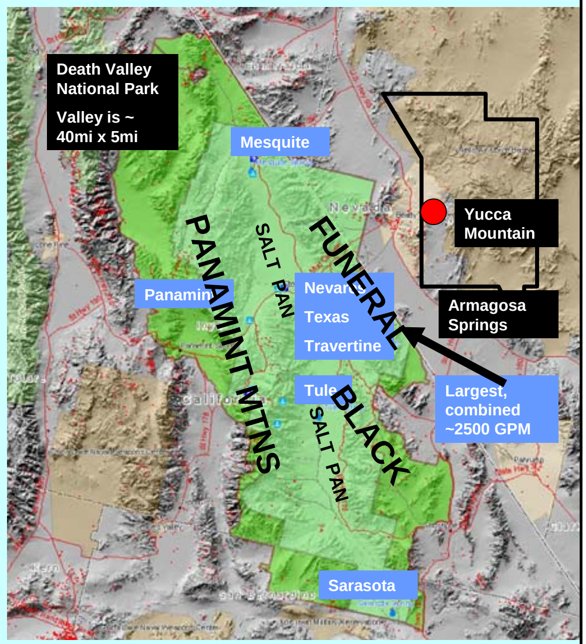
4 Types of Springs:

Springs along
Steeply Dipping Faults
Major springs 1000s GPM, between Funeral/Black Mtns

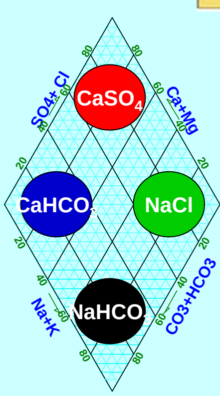
Mountain Springs
minor 0-20GPM,
high elevation,
along intermittent creeks

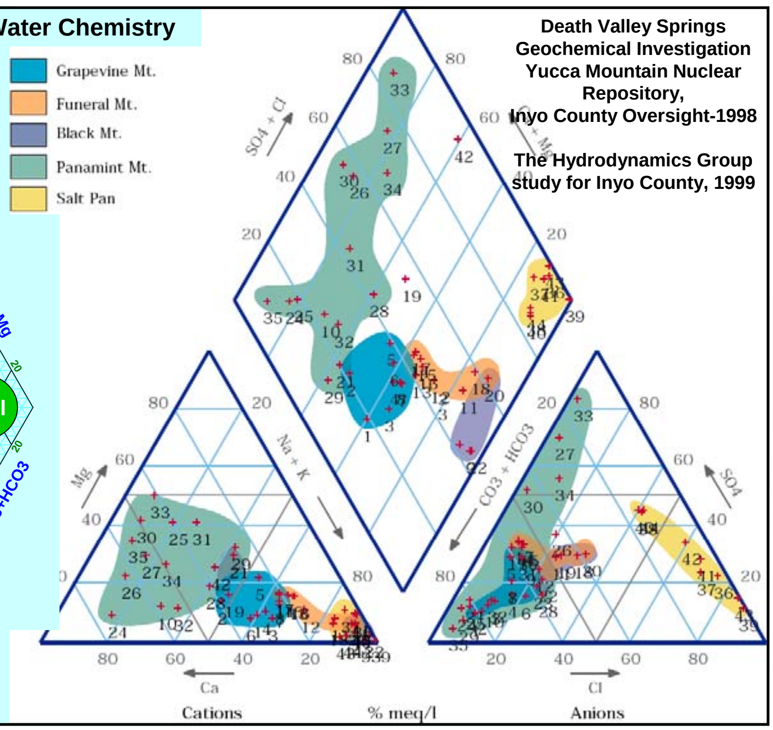
Springs at
Impermeable Structural Barriers
few & minor ~10GPM

Springs at the
Edge of Alluvial Fans
Base of Panamint at Salt Pan



Death Valley Water Chemistry





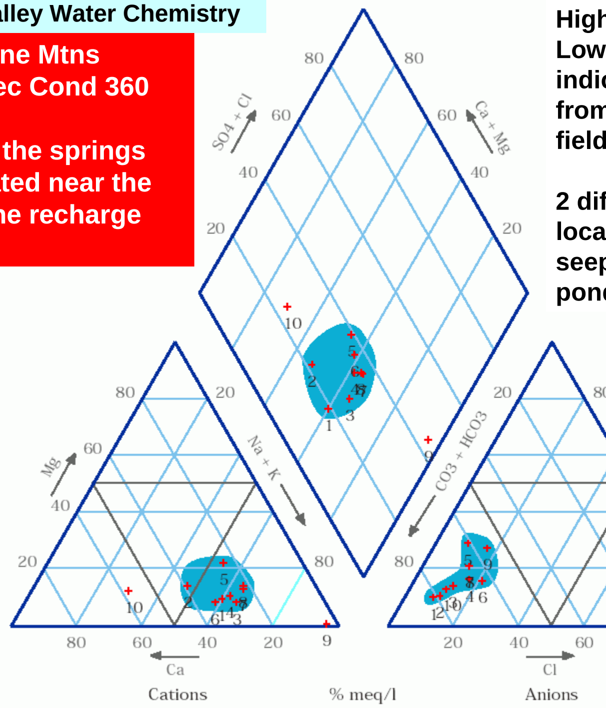
Death Valley Springs Geochemical Investigation Yucca Mountain Nuclear Repository, Inyo County Oversight-1998

The Hydrodynamics Group study for Inyo County, 1999

Death Valley Water Chemistry

Grapevine Mtns
Avg Spec Cond 360

Most of the springs are located near the top of the recharge system



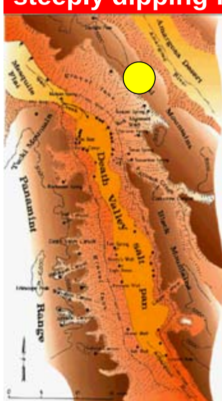
High HCO_3^-
Low Cl^- SO_4^- Mg^{+2} indicate young GW from nearby snow fields

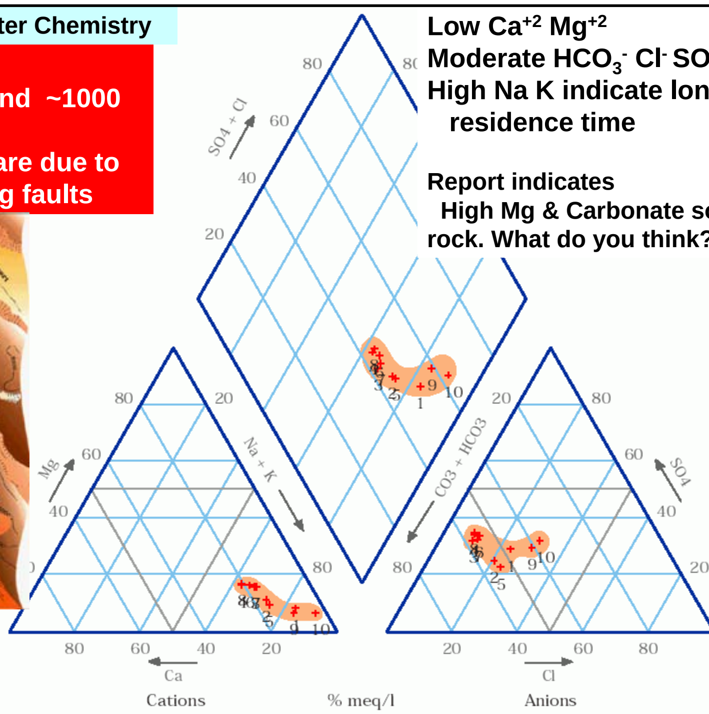
2 differ - they are localized intermittent seeps where water ponds & evaporates

Death Valley Water Chemistry

Funeral Mtns
Avg Spec Cond ~1000

Most springs are due to steeply dipping faults





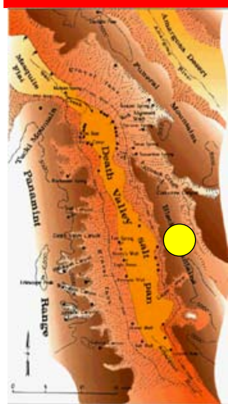
Low Ca^{+2} Mg^{+2}
Moderate HCO_3^- Cl^- SO_4^-
High Na K indicate long residence time

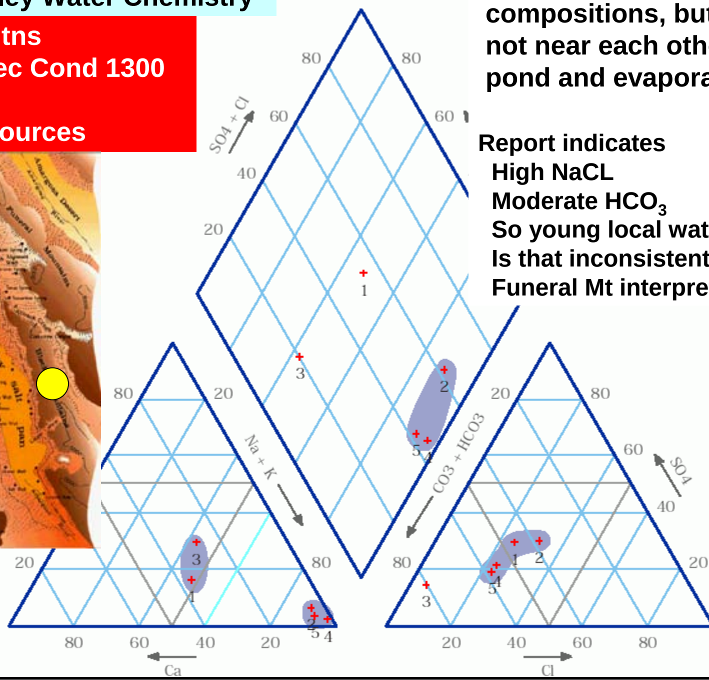
Report indicates High Mg & Carbonate sour rock. What do you think?

Death Valley Water Chemistry

Black Mtns
Avg Spec Cond 1300

Mixed sources





 # 2 4 5 have similar compositions, but are not near each other, all pond and evaporate

Report indicates
High NaCL
Moderate HCO_3
So young local water
Is that inconsistent with
Funeral Mt interpretation?

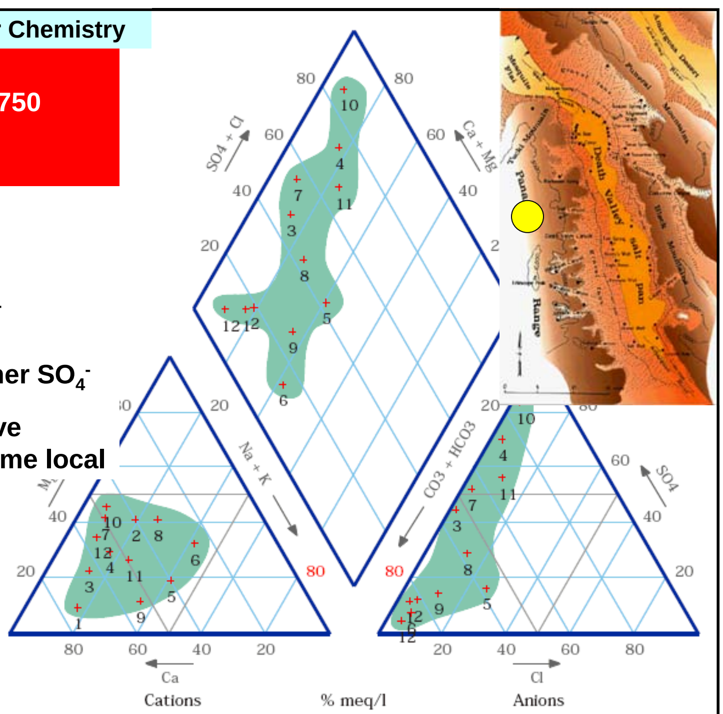
Death Valley Water Chemistry

Panamint Mtns
Avg Spec Cond 750

Mixed sources

High Ca^{+2}
Moderate Mg^{+2}
Wide range of
Na^{+} Cl^{-} HCO_3^{-} SO_4^{-}
Older waters are
Lower HCO_3^{-} Higher SO_4^{-}

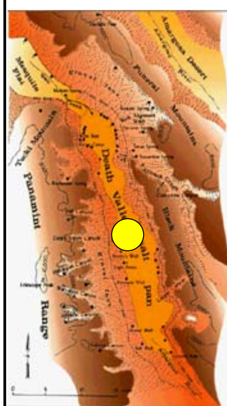
Some springs have deep source & some local

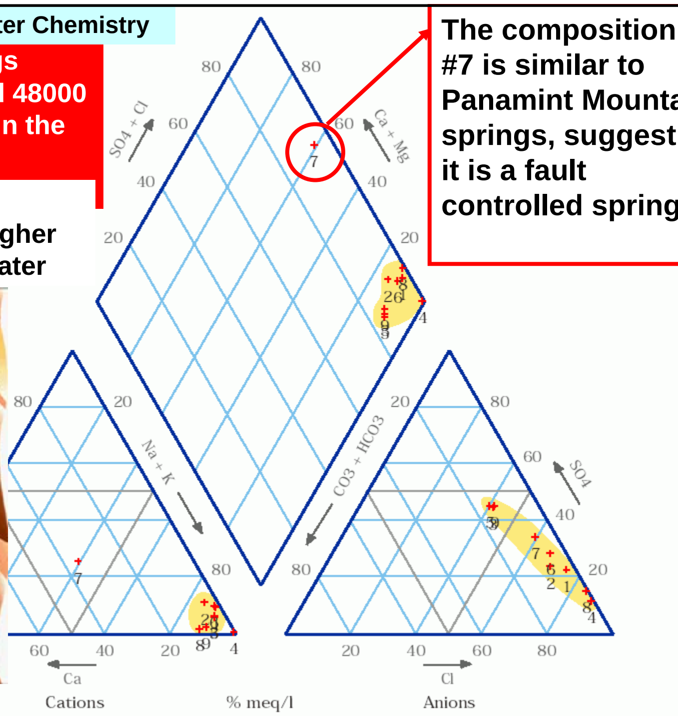


Death Valley Water Chemistry

Salt Pan springs
Avg Spec Cond 48000
At the edge or in the valley

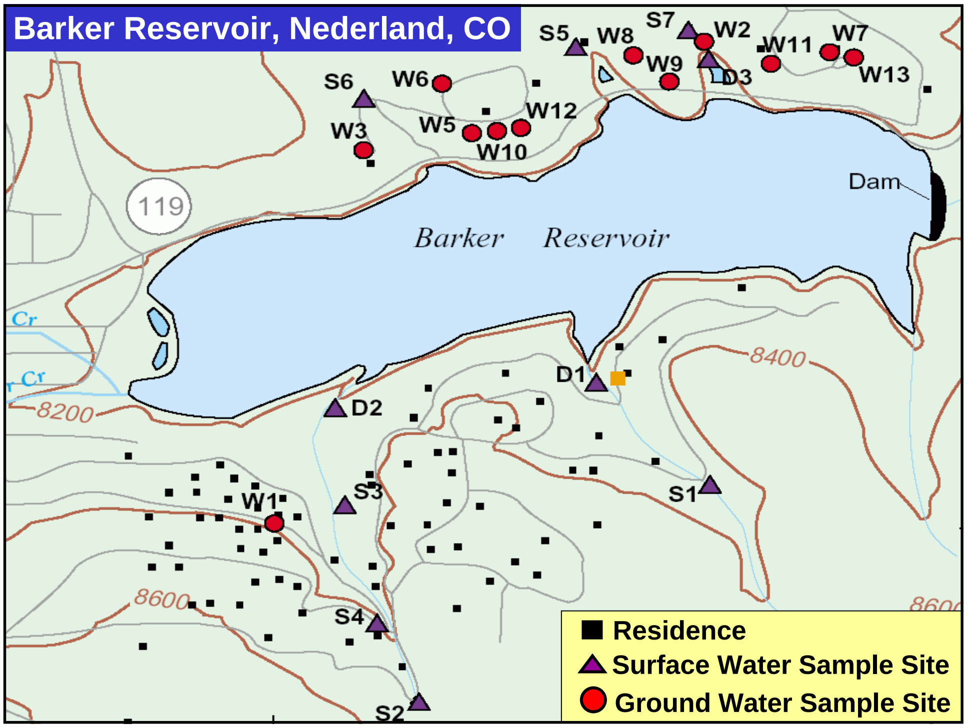
Dominated by evaporation: higher NaCl than sea water





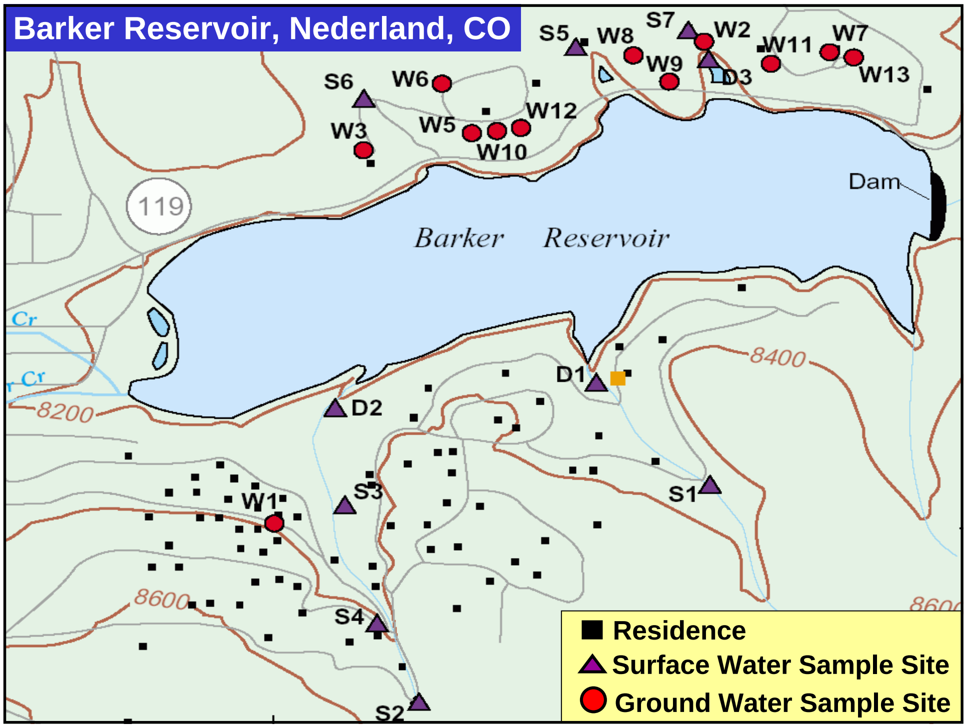
The composition of #7 is similar to Panamint Mountain springs, suggesting it is a fault controlled spring

Did the Geochemical Study Resolve the Question?

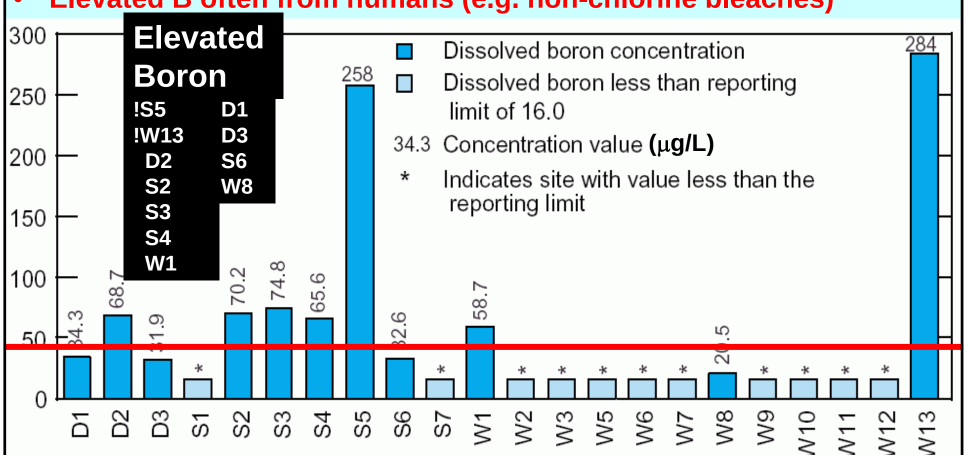


Barker Reservoir, Nederland, CO
USGS OFR 00-214, 2000

- **Supplies 40% of drinking water for Boulder, CO**
- **Primarily Precambrian igneous and metamorphic rock, except for Quaternary deposits in drainages**
- **Ground water inflow passes beneath residential developments on the north and south sides of the reservoir**
- **Homes near reservoir use individual wastewater disposal systems**
- **USGS & City of Boulder studied to evaluate impact of sewage disposal systems on Barker Reservoir**



- Boron (B) is a good indicator of sewage disposal system impact
  1) natural concentrations are generally low relative to effluent
  2) B does not undergo biological removal during treatment, and
  3) B is not significantly sorbed to soil or rocks
- B typically <10 μg/L to 40 μg/L
- Elevated B often from humans (e.g. non-chlorine bleaches)



Dissolved boron concentrations in ground water and surface water

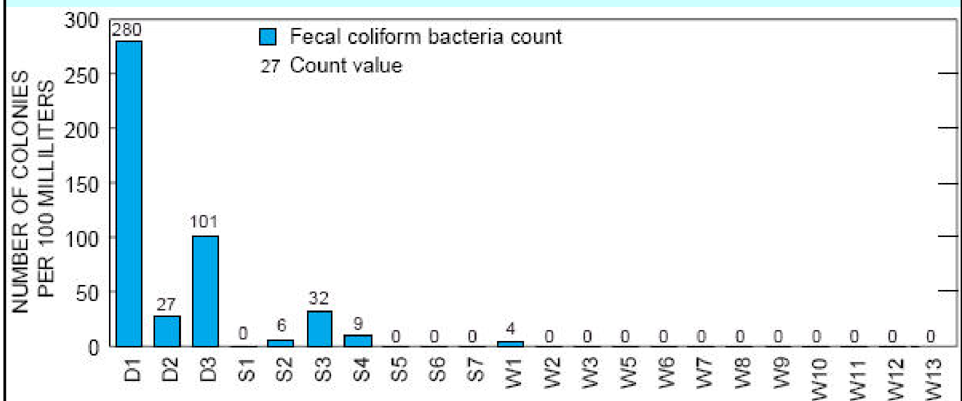
Elevated Fecal Coliforms

!D1
!D3
D2
S2
S3
S4
W1

Elevated Boron. Red indicates those that also show up with elevated coliforms. Perhaps the very high B in some samples reduced micro-organisms

!S5
!W13
D2
S2
S3
S4
W1

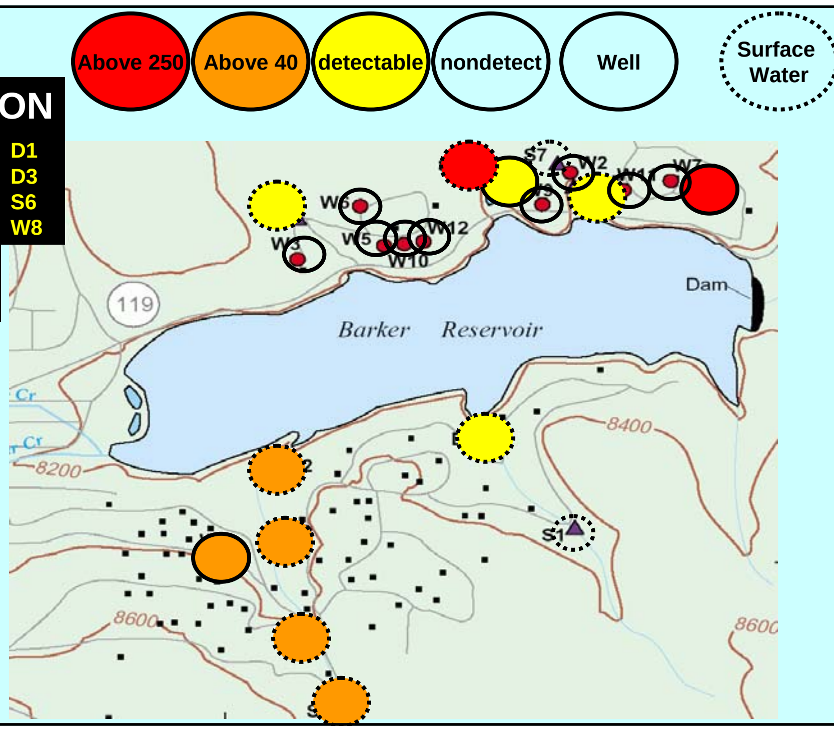
D1
D3
S6
W8

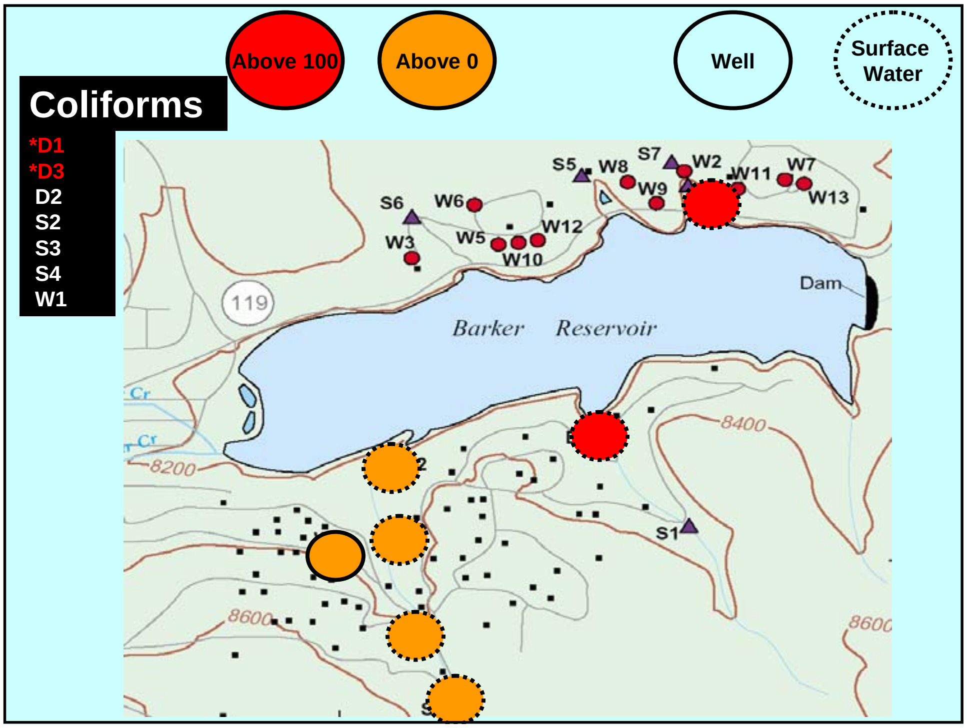


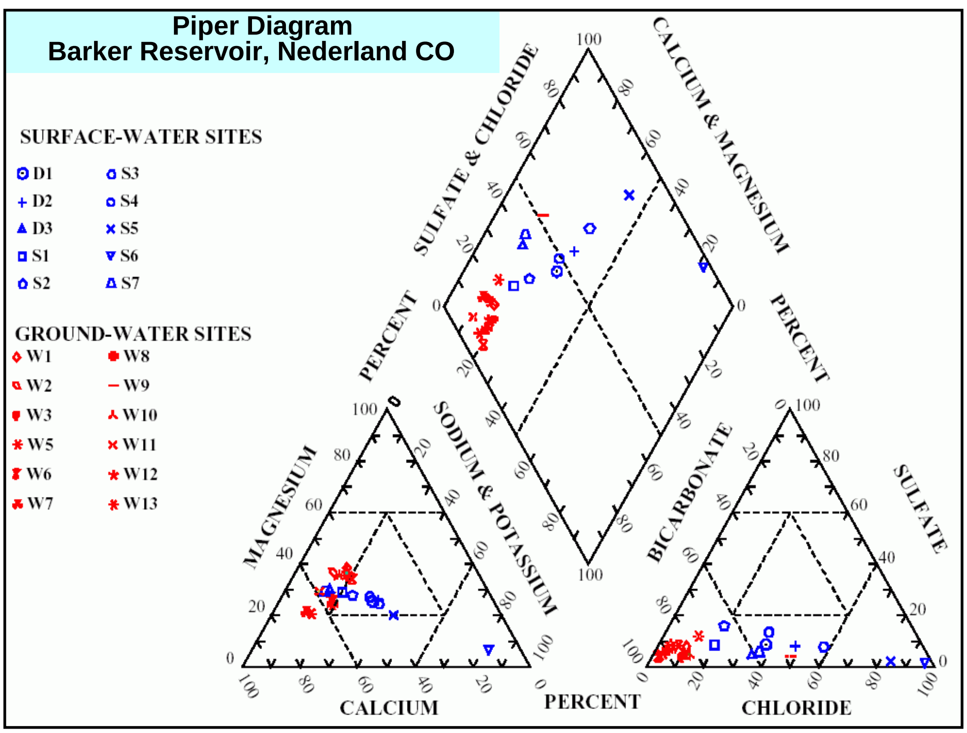
BORON

*S5
*W13
D2
S2
S3
S4
W1

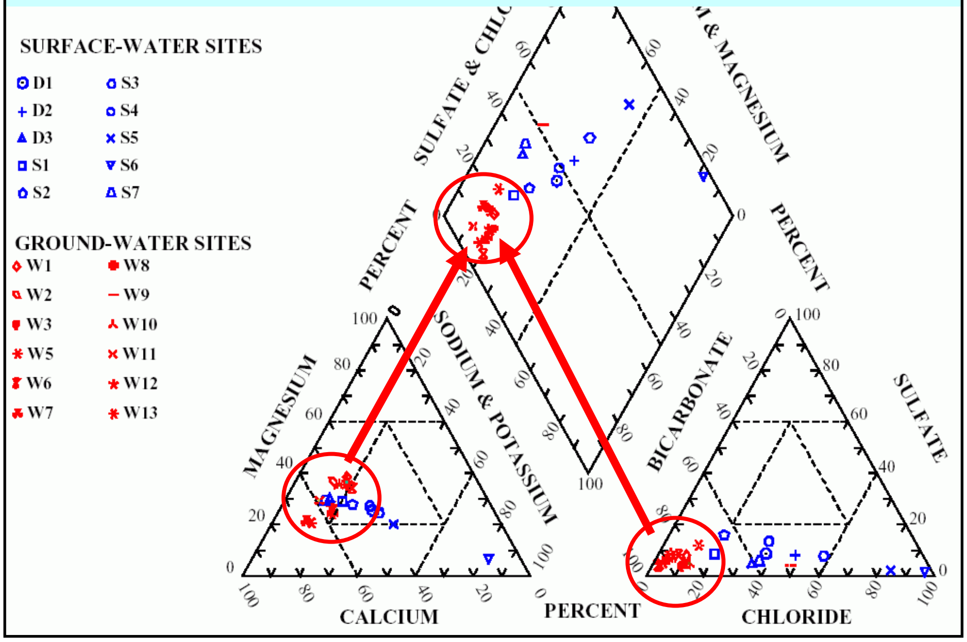
D1
D3
S6
W8



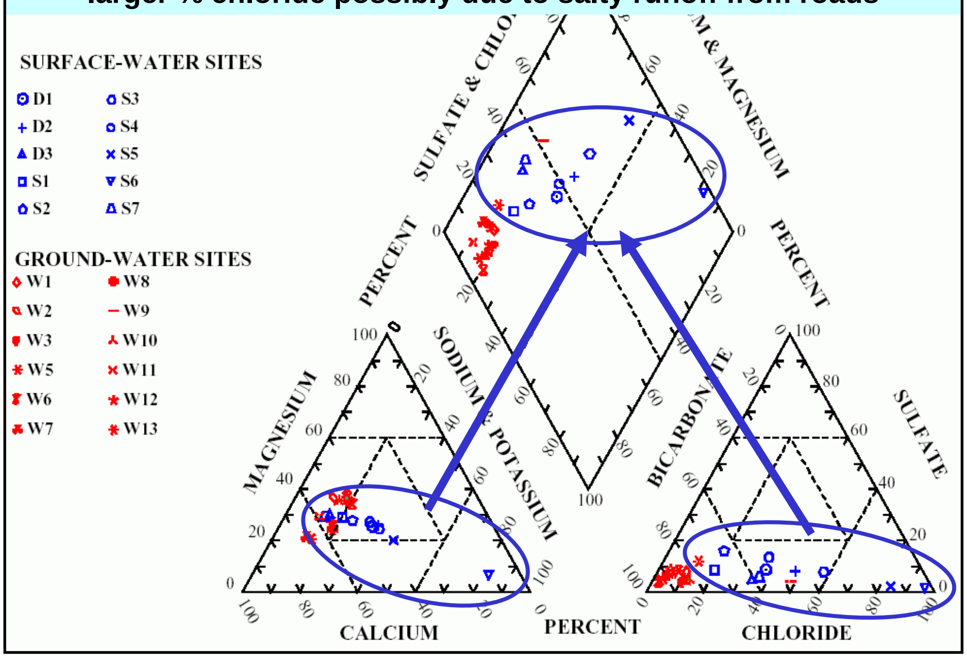

Above 100
Above 0
Well
Surface Water
Coliforms
*D1
*D3
D2
S2
S3
S4
W1
S5
W8
S7
W2
W11
W7
W13
S6
W6
W9
W3
W5
W10
W12
119
Dam
Barker Reservoir
Cr
Cr
8200
8400
S1
8600
8600


Piper Diagram
Barker Reservoir, Nederland CO
SURFACE-WATER SITES
D1
S3
D2
S4
D3
S5
S1
S6
S2
S7
GROUND-WATER SITES
W1
W8
W2
W9
W3
W10
W5
W11
W6
W12
W7
W13
SULFATE & CHLORIDE
CALCIUM & MAGNESIUM
PERCENT
PERCENT
SODIUM & POTASSIUM
BICARBONATE
MAGNESIUM
SULFATE
CALCIUM
PERCENT
CHLORIDE

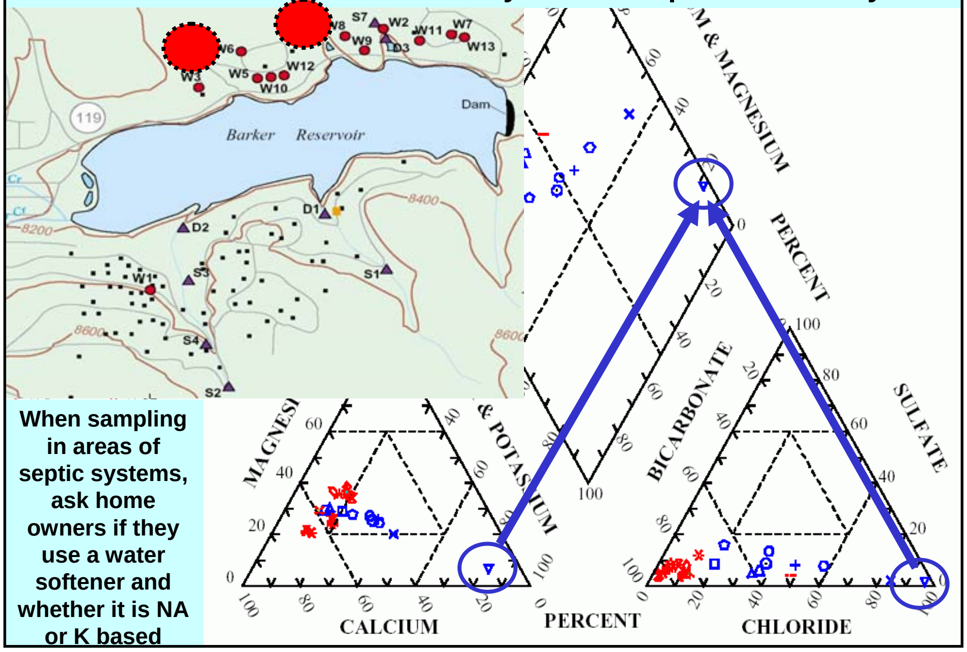
Clustered samples indicate similar ion ratios
Ground waters are calcium-bicarbonate type



Surface-water samples are less similar than ground water and have larger % chloride possibly due to salty runoff from roads

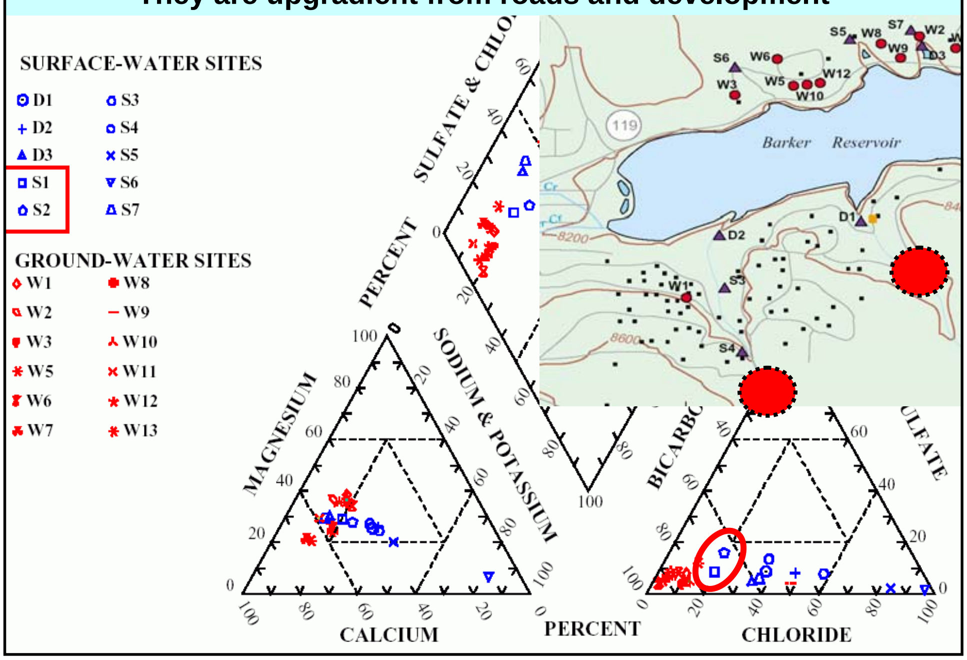


Site S6 & S5 - high % sodium & chloride
ion ratios are not similar to any other sample in the study



When sampling in areas of septic systems, ask home owners if they use a water softener and whether it is NA or K based

S1 & S2 have lower chloride % than other surface-water samples
They are upgradient from roads and development



On-Site Waste Water Systems
Barker Reservoir, Nederland, CO
USGS OFR 00-214, 2000

Conclusions:

GW north of reservoir was not extensively contaminated

Contaminated sites were associated with older developed areas, so time may be a factor

South of the reservoir downgradient SW is contaminated but it could be from wildlife and domestic animals

More well samples are needed

ACID MINE DRAINAGE (AMD)

When mining involves lowering the water table, it exposes rocks to oxygen

Pyrite FeS_2 + air + water produces
sulfuric acid H_2SO_4 &
iron hydroxide $Fe(OH)_3$

A visible sign may be iron hydroxide on stream bottoms "yellow boy"

The acid runoff dissolves heavy metals such as copper, lead, mercury

San Juan Mountains, Colorado

Southern Stark County, Ohio
Bear Creek Run Watershed

Miller and Foos, North Central GSA 199

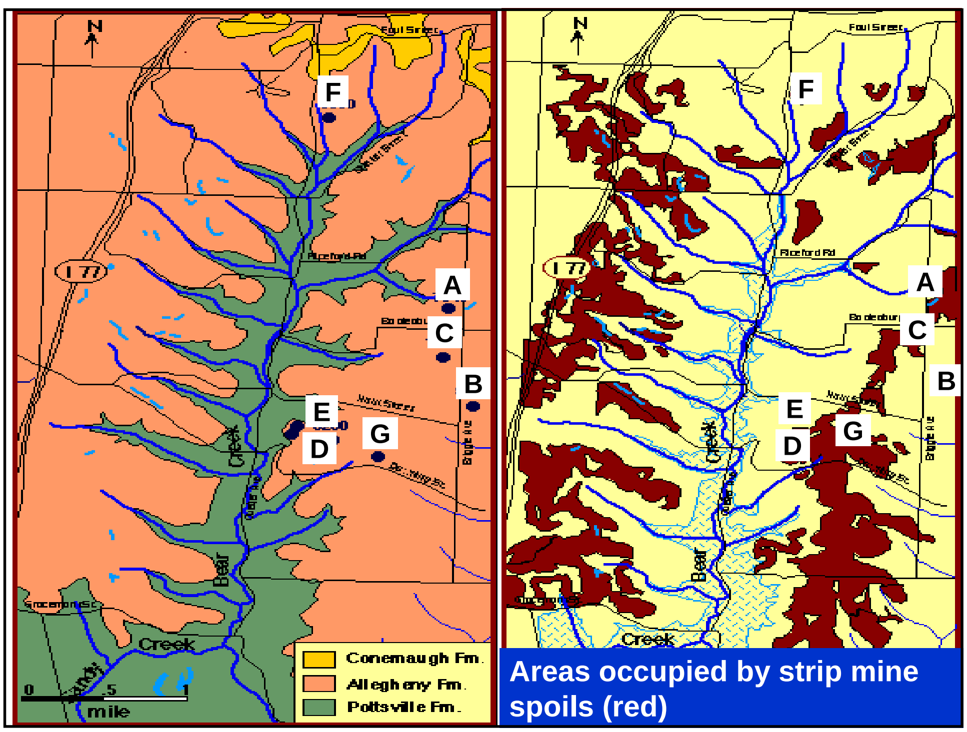
- **Unglaciated area**
- **relief up to 200 feet per 0.5 miles**
- **3 Pennsylvanian aged units**

  Conemaugh, Allegheny, and Pottsville Formations

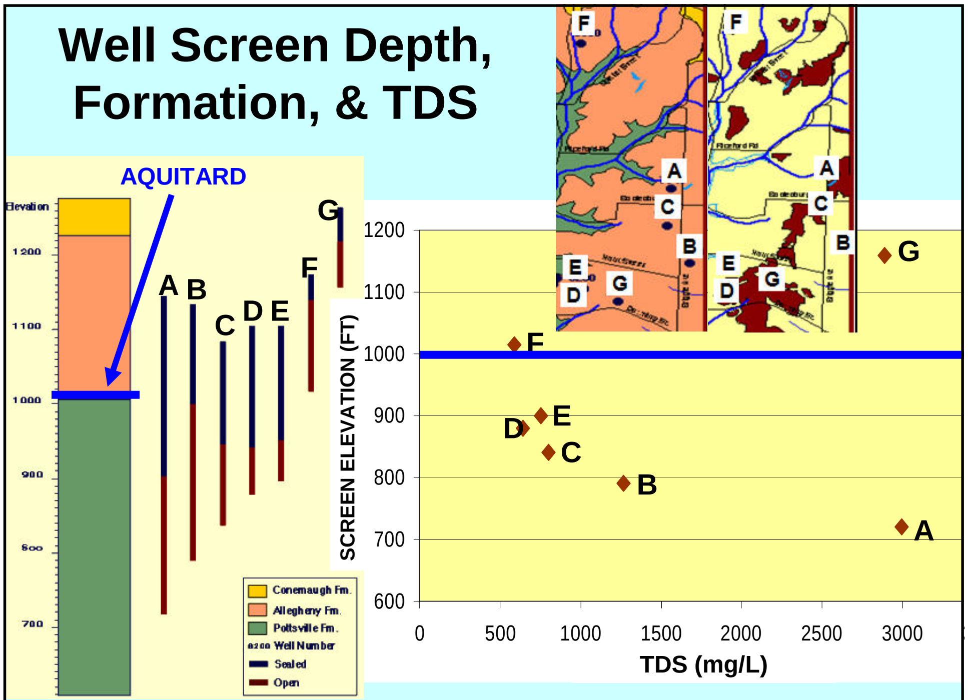
  interbedded coals, shales, and limestone

  Brookville Underclay is a major regional aquitard

  between Allegheny and Pottsville Formations
- **Area was strip mined for coal and limestones for most of the 20th century**
- **Abandoned mine spoils occupy approximately 40% of the drainage basin**



Well Screen Depth, Formation, & TDS



Sample Data (C in mg/L)

	A	B	C	D	E	F	G
Temp	12.0	11.7	11.7	10.6	11.5	12.1	11.2
pH	7.46	8.42	8.60	7.04	7.55	7.17	4.89
HCO3	876	776	552	424	512	324	28
CO3	0	67	0	0	0	0	0
Cl	1266.4	72.9	10.4	43.1	32.5	15.9	8.7
SO4	<10	<10	10.9	<10	<10	82.4	2069.9
PO4	0.15	0.75	0.55	0.10	0.20	0.18	0.10
N	0.26	0.18	0.22	0.31	0.40	0.44	0.26
Br	11.50	1.20	0.06	0.60	0.44	0.13	0.04
Na	890	340	220	140	190	160	20
K	8.5	3.0	2.3	7.2	5.0	2.1	5.6
Mg	6.21	0.36	0.18	7.43	3.99	0.70	223.50
Ca	20	0.8	0.6	22	12	2	443
Al	0.13	0.13	0.13	0.13	0.11	0.13	5.40
Mn	0.01	0	0	0.03	0.02	0.01	46.1
Fe	0	0.01	0.01	0.02	0.01	0.02	46.7
Si	3.4	3.3	3.4	3.1	3.1	3.3	ND
TDS	2996	1264	800	645	757	590	2890

Sample Data (C in mg/L)

exceeds secondary standards … there are no primary standards for those items

	A	B	C	D	E	F	G
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PO4	0.15	0.75	0.55	0.10	0.20	0.18	0.10
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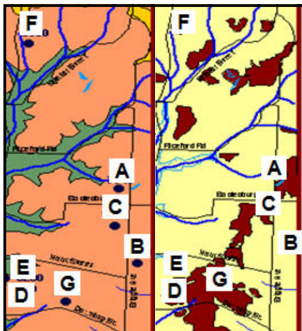
Br	11.50	1.20	0.06	0.60	0.44	0.13	0.04
Na	890	340	220	140	190	160	20
K	8.5	3.0	2.3	7.2	5.0	2.1	5.6
Mg	6.21	0.36	0.18	7.43	3.99	0.70	223.50
Ca	20	0.8	0.6	22	12	2	443
Al	0.13	0.13	0.13	0.13	0.11	0.13	5.40
Mn	0.01	0	0	0.03	0.02	0.01	46.1
Fe	0	0.01	0.01	0.02	0.01	0.02	46.7
Si	3.4	3.3	3.4	3.1	3.1	3.3	ND
TDS	2996	1264	800	645	757	590	2890

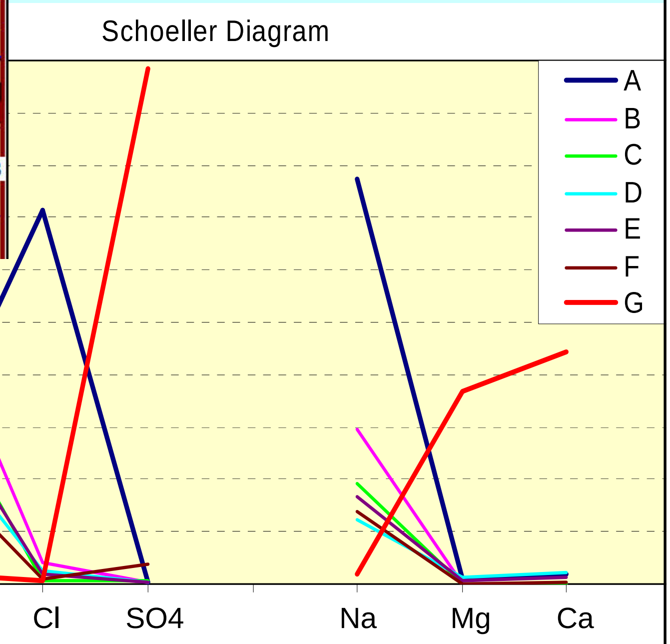
Secondary Maximum Contaminant Levels

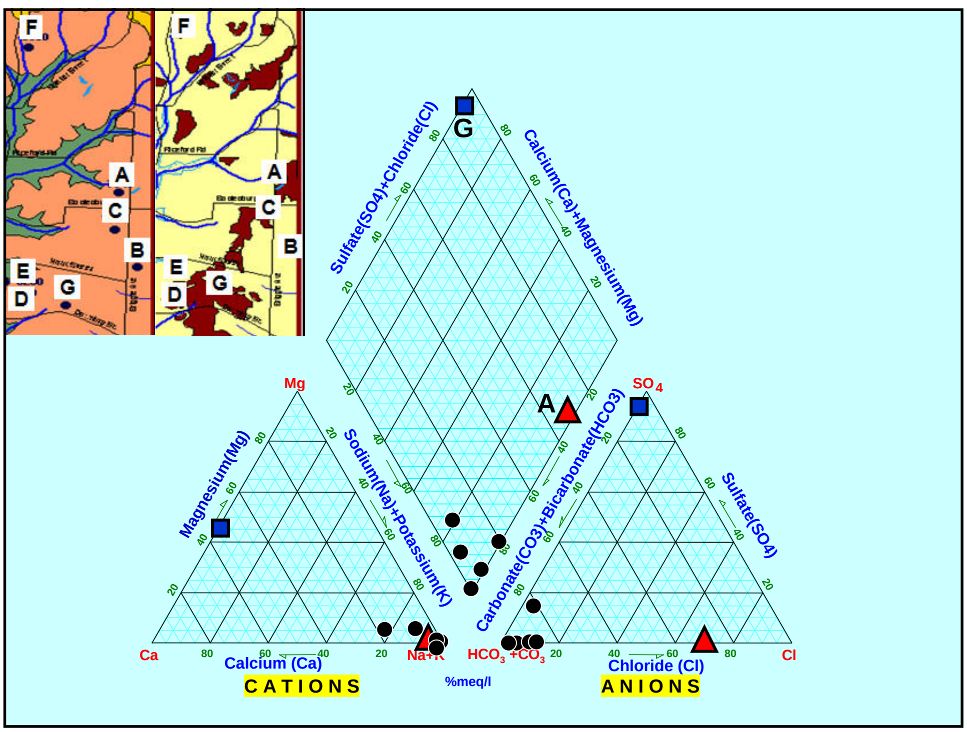
Contaminant	Secondary MCL	Noticeable Effects above the Secondary MCL
Aluminum	0.05 to 0.2 mg/L*	colored water
Chloride	250 mg/L	salty taste
Color	15 color units	visible tint
Copper	1.0 mg/L	metallic taste; blue-green staining
Corrosivity	Non-corrosive	metallic taste; corroded pipes/ fixtures staining
Fluoride	2.0 mg/L	tooth discoloration
Foaming agents	0.5 mg/L	frothy, cloudy; bitter taste; odor
Iron	0.3 mg/L	rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	black to brown color; black staining; bitter metallic taste
Odor	3 TON (threshold odor number)	"rotten-egg", musty or chemical smell
pH	6.5 - 8.5	*low pH:* bitter metallic taste; corrosion *high pH:* slippery feel; soda taste; deposits
Silver	0.1 mg/L	skin discoloration; graying of the white part of the eye
Sulfate	250 mg/L	salty taste
Total Dissolved Solids (TDS)	500 mg/L	hardness; deposits; colored water; staining; salty taste
Zinc	5 mg/L	metallic taste

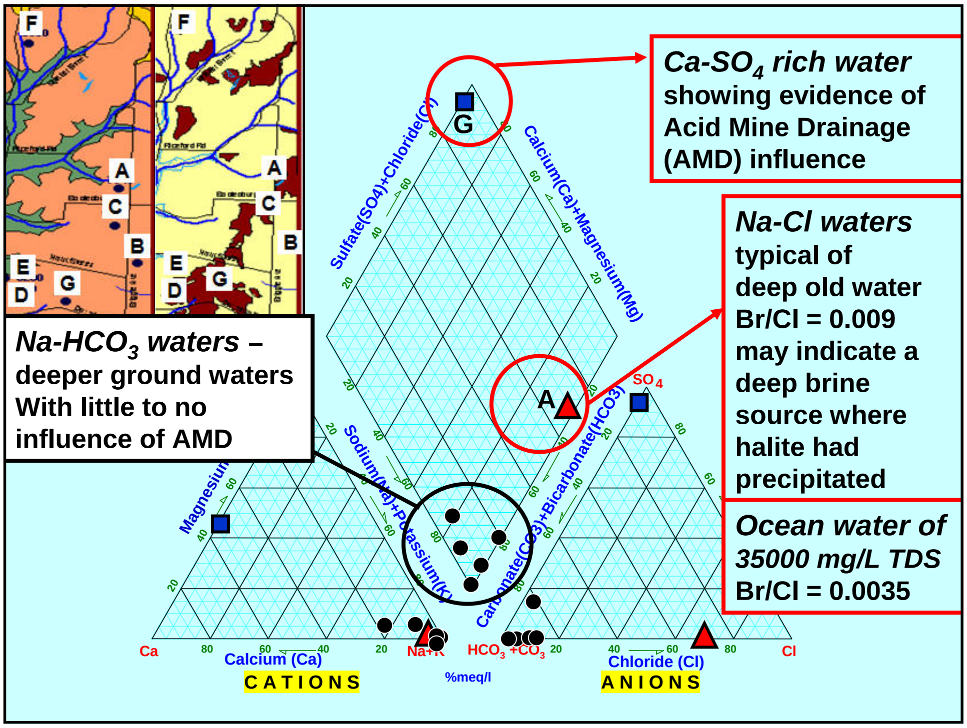
** mg/L is milligrams of substance per liter of water*

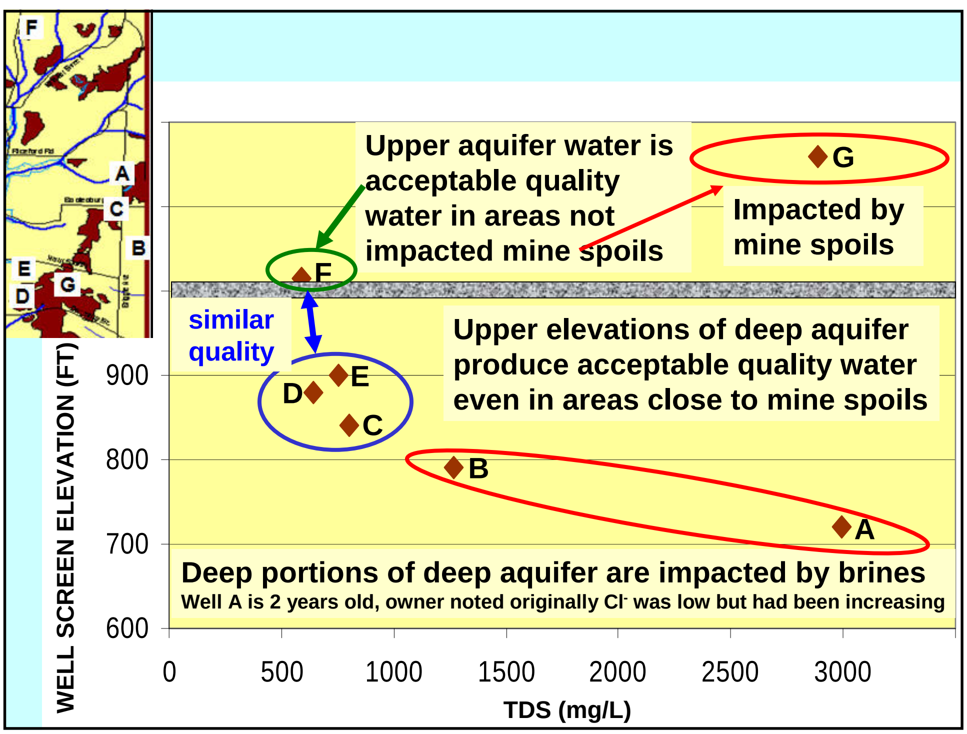
Wells A and G are Distinct








Ca-SO4 rich water showing evidence of Acid Mine Drainage (AMD) influence
Na-Cl waters typical of deep old water Br/Cl = 0.009 may indicate a deep brine source where halite had precipitated
Ocean water of 35000 mg/L TDS Br/Cl = 0.0035
Na-HCO3 waters – deeper ground waters With little to no influence of AMD
Sulfate(SO4)+Chloride(Cl)
Calcium(Ca)+Magnesium(Mg)
Sodium(Na)+Potassium(K)
Carbonate(CO3)+Bicarbonate(HCO3)
Magnesium
Calcium (Ca)
Chloride (Cl)
CATIONS
ANIONS
%meq/l
Ca
Na+K
HCO3 +CO3
Cl
SO4
A
B
C
D
E
F
G


Upper aquifer water is acceptable quality water in areas not impacted mine spoils
Impacted by mine spoils
similar quality
Upper elevations of deep aquifer produce acceptable quality water even in areas close to mine spoils
Deep portions of deep aquifer are impacted by brines
Well A is 2 years old, owner noted originally Cl- was low but had been increasing
WELL SCREEN ELEVATION (FT)
TDS (mg/L)
600
700
800
900
0
500
1000
1500
2000
2500
3000
A
B
C
D
E
F
G