

## Presentation #2

- Groundwater geochemistry, uses data from U.S Geological Survey Open-File Report 2012-1070
  - Johnson, R.H., 2012, Geochemical data from groundwater at the proposed Dewey Burdock uranium in-situ recovery mine, Edgemont, South Dakota: U.S. Geological Survey, Open-File Report 2012–1070, 11 p.  
(<http://pubs.usgs.gov/of/2012/1070/>)
- Presentation to the EPA on February 22, 2012



# Update on USGS research at the Proposed Dewey Burdock Uranium In-Situ Recovery Mine, Edgemont, South Dakota

By Raymond H. Johnson



## Project Goal

- Demonstrate how reactive transport modeling can be used as a tool to assess future influences of uranium in-situ recovery (ISR) mining on groundwater geochemistry
  - First need to thoroughly understand the current system
  - Then add details to reactive transport



Before doing more detailed reactive transport modeling, this presentation presents information on the current groundwater flow system based on groundwater geochemistry.

## This presentation

- Summarize results of new USGS groundwater data collection (June 2011)



These data were collected to support better understanding of the current groundwater flow system and to use in more detailed reactive transport (presentation #5 in this series).

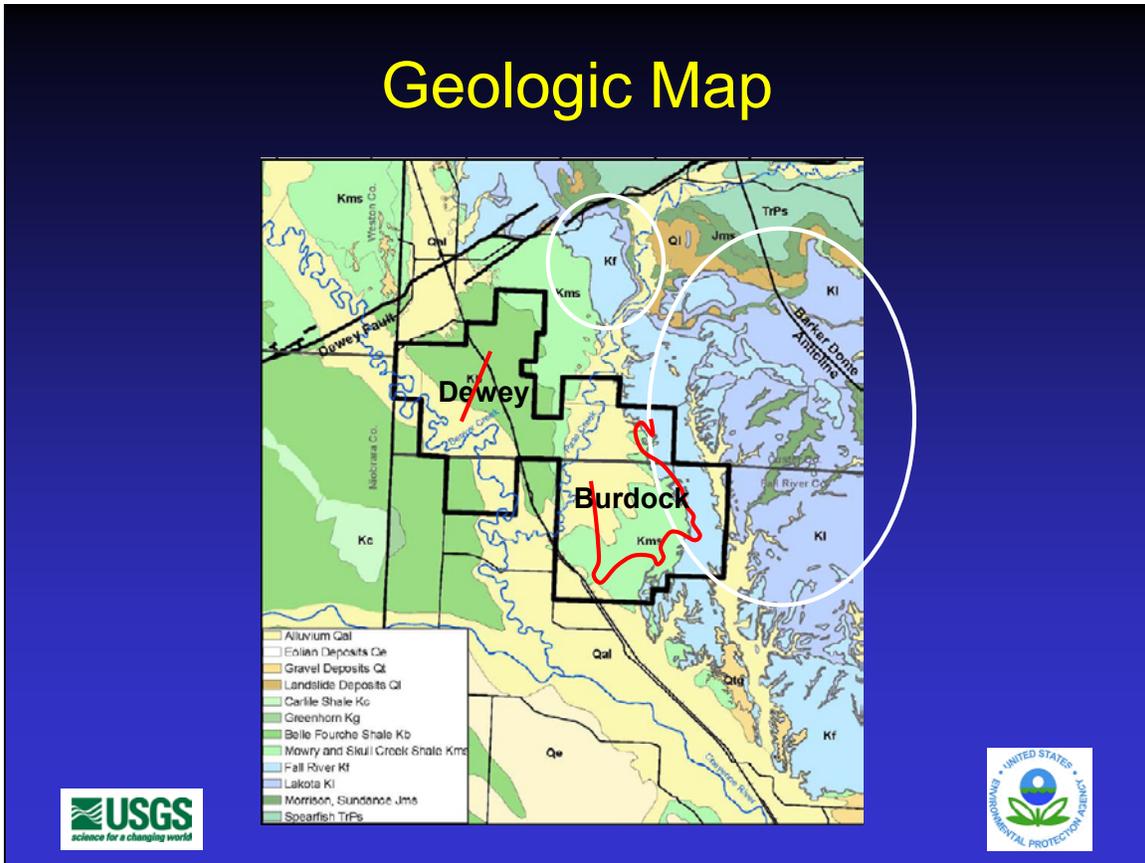
## Groundwater Geochemistry

- Field parameters (temp., pH, pe, DO, cond.)
- Cations and dissolved metals
- Anions (sulfate, chloride, fluoride)
- Uranium isotopes and uranium concentration
- Dissolved organic carbon
- Iron species
- Tritium
- Water isotopes ( $^{18}\text{O}$  and D)
- $^{34}\text{S}$
- $^{14}\text{C}$  – 6 samples sent on Jan. 10, 2012



This is the list of the types of groundwater geochemistry data that were collected. In the following slides, an introduction slide is included for each constituent on how it is used for interpretations.

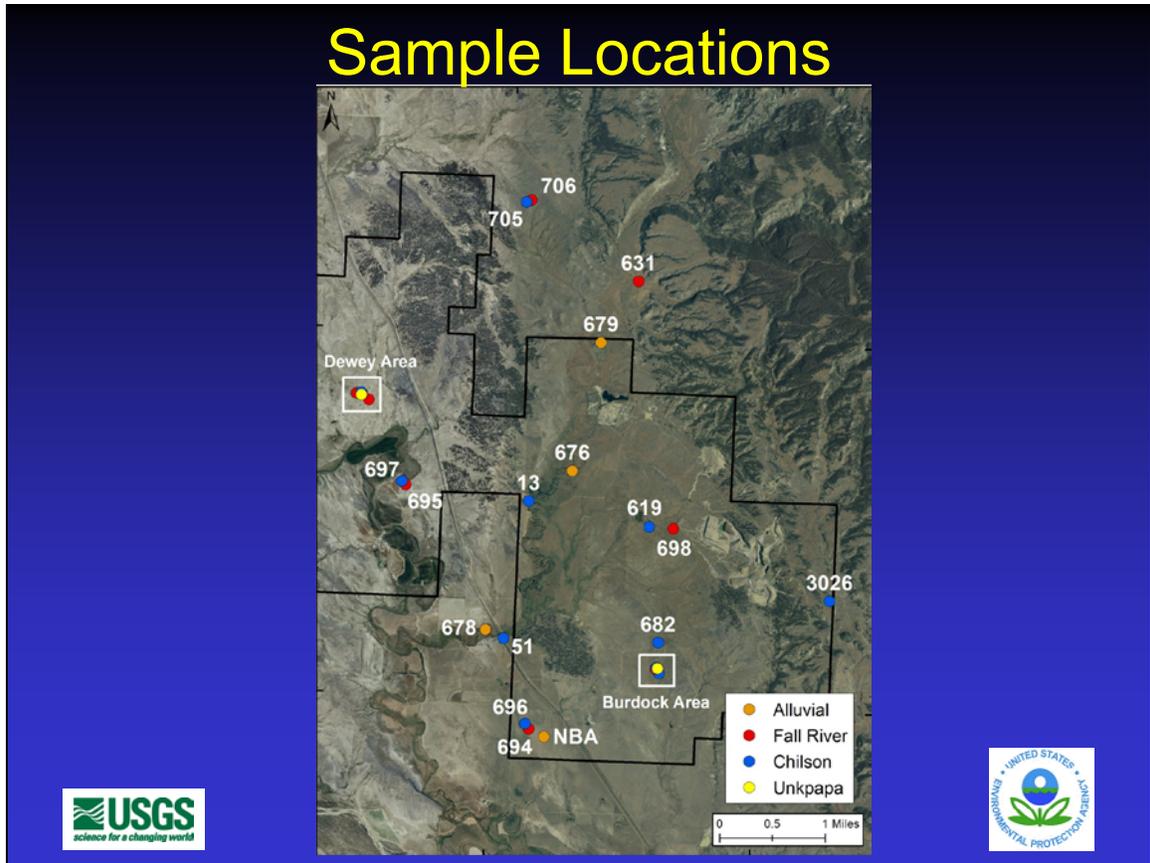
## Geologic Map



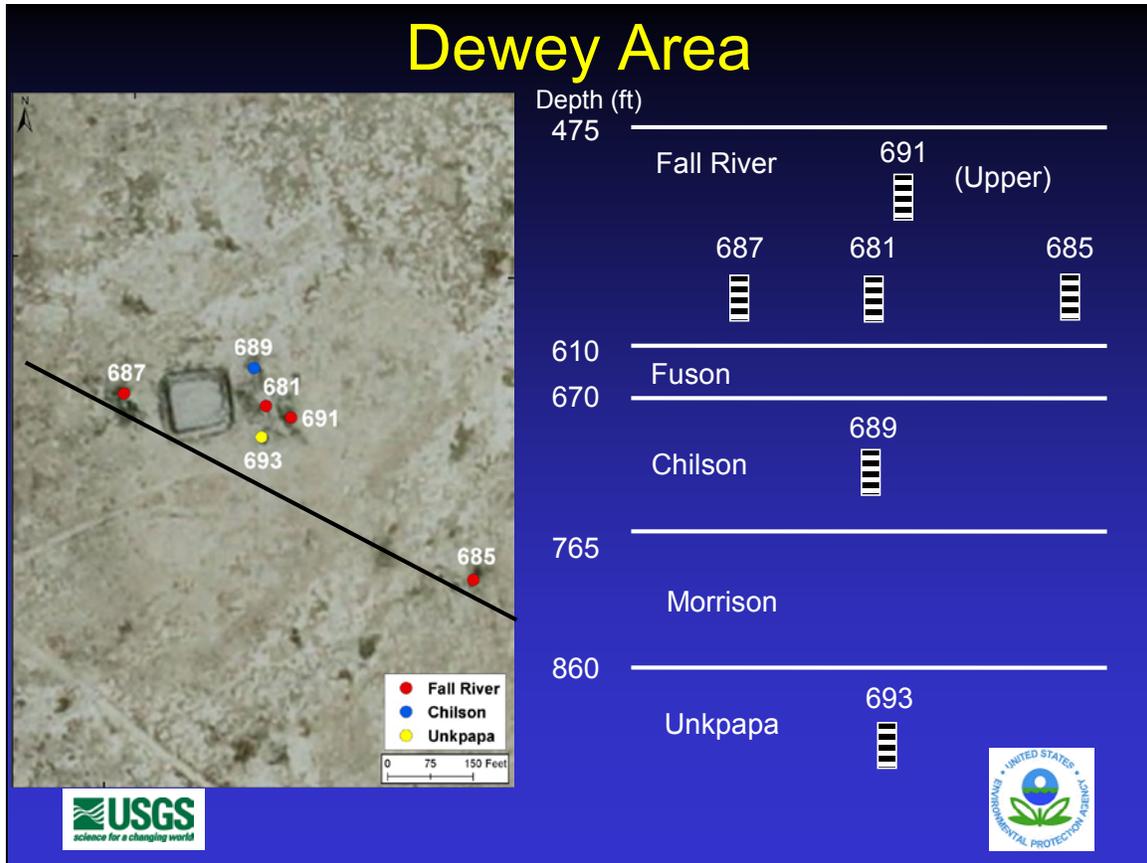
The white circles indicate the recharge zone for the Fall River Formation (left) and the Lakota Formation (right).

The Fall River recharge area is quite small and close to Pass Creek; whereas, the Lakota recharge area is much larger and forms a separate drainage area.

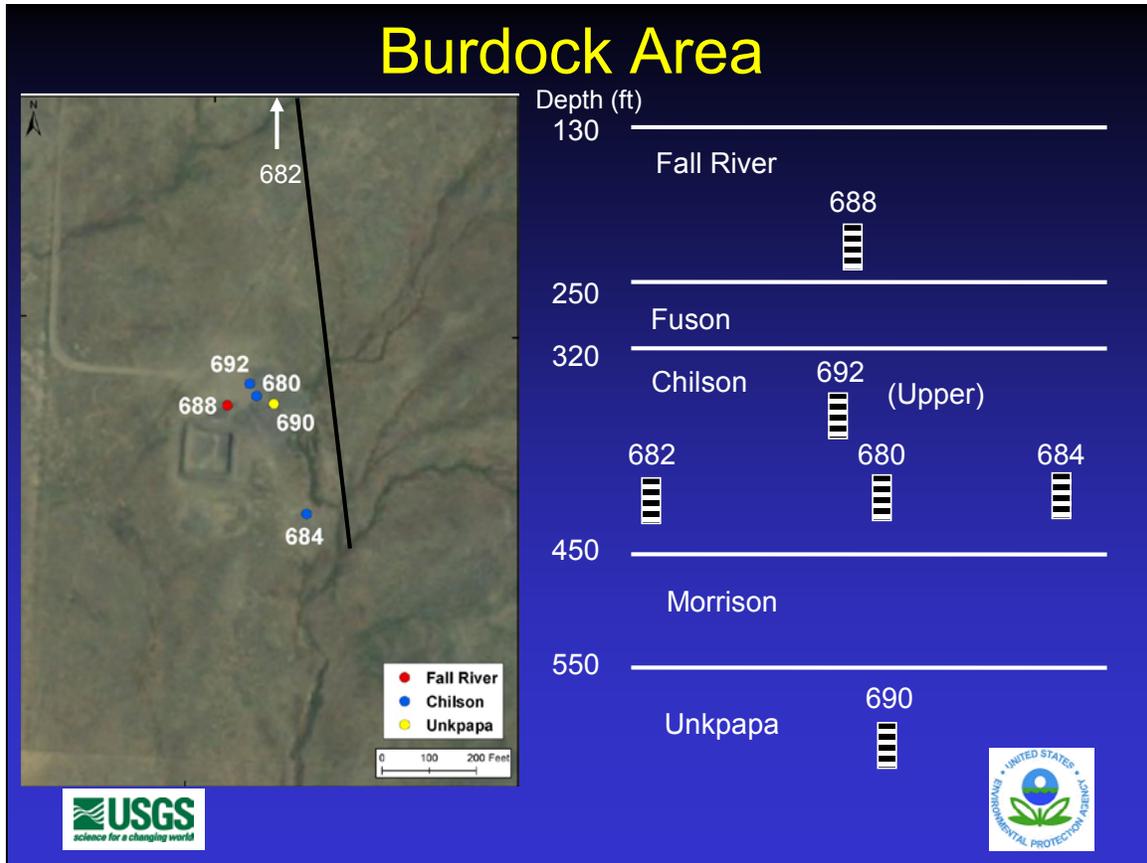
Red lines indicate ore zones. Dewey area is in the Fall River Formation and Burdock area is in the Lower Chilson Member of the Lakota Formation.



All of these sample locations are from existing wells. Locations were selected to get a good overall area representation.



In this and subsequent slides, the map is a plan view of the area and the black line represents the cross section location, with the cross section shown on the right. The depths on the cross section are approximately to scale, with an indication of formation name, well number, and well screen interval.



Location of well 682 is shown in slide #7.

## Tritium

- Tritium was added to the atmosphere during nuclear weapons testing
- Detectable tritium = water that is younger than 60 years old
- Tritium is not reactive
- Error (1 SD) of about +/- 0.5 to 0.6 TU
- Tritium contamination during TVA exploration is a possibility

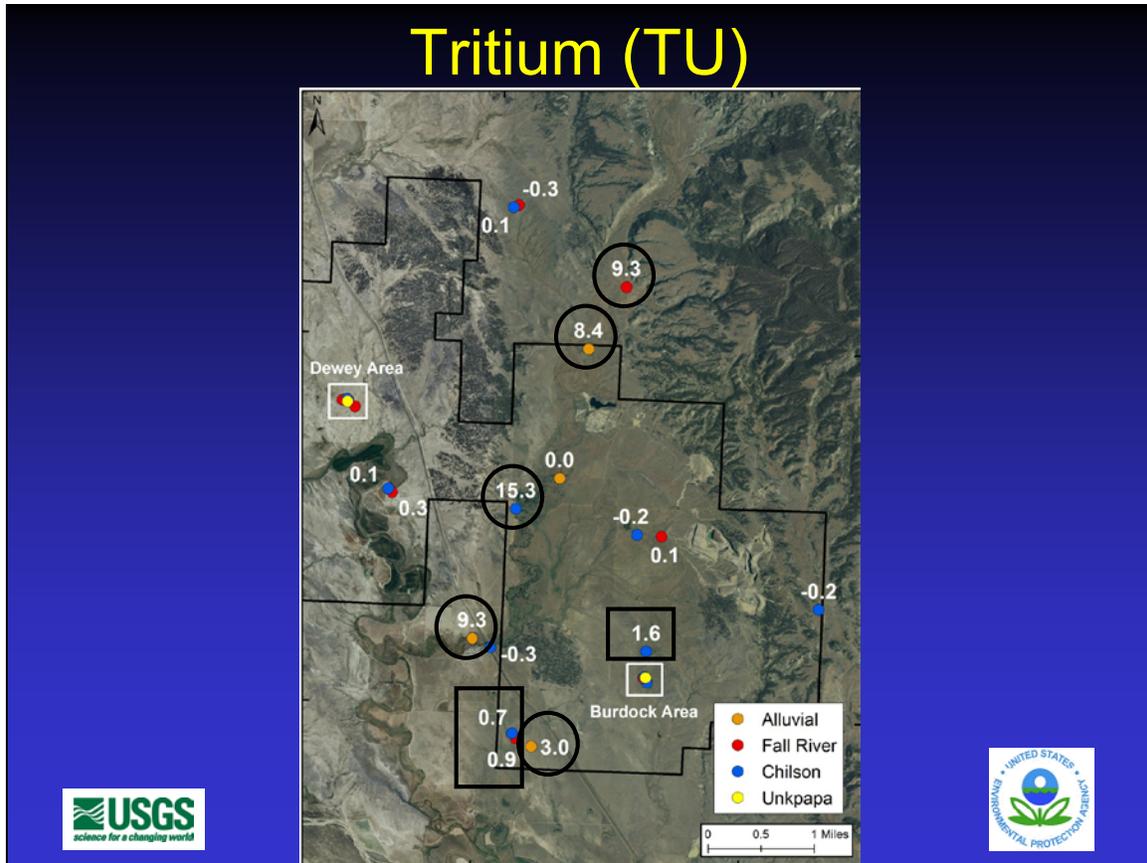


SD = standard deviation.

TU = tritium units.

If no tritium – 60 years old or older.

If some tritium – possibility that it could be older because of contamination during TVA (Tennessee Valley Authority) exploration.

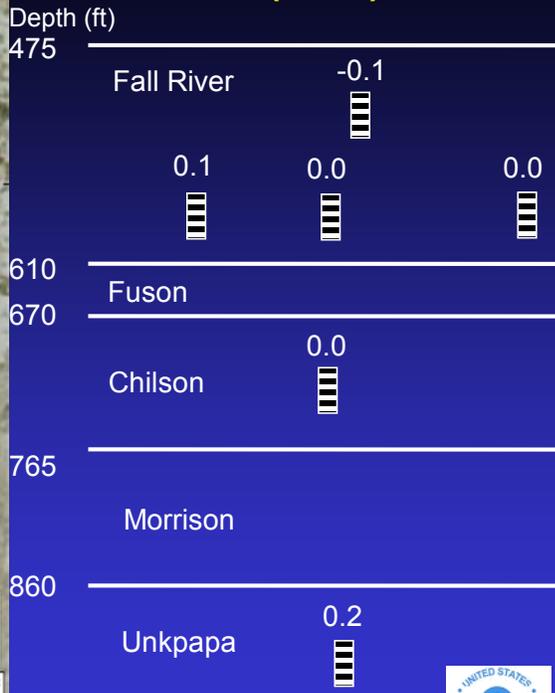


The circles indicate wells with tritium that likely indicate recent recharge (less than 60 years old).

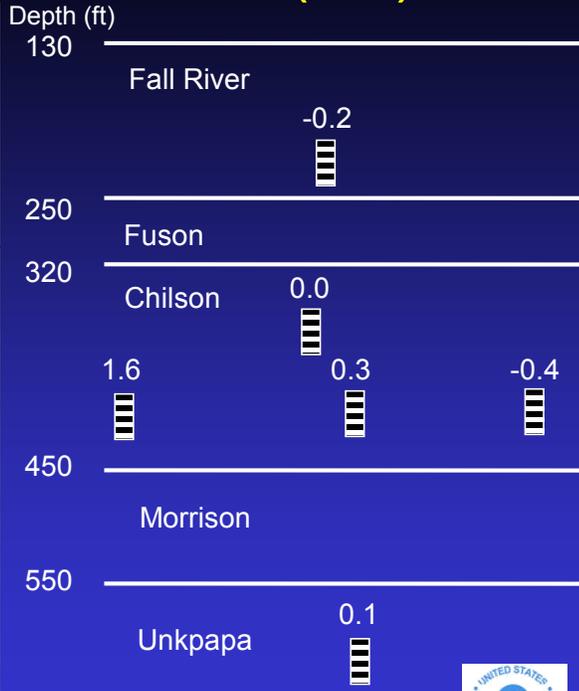
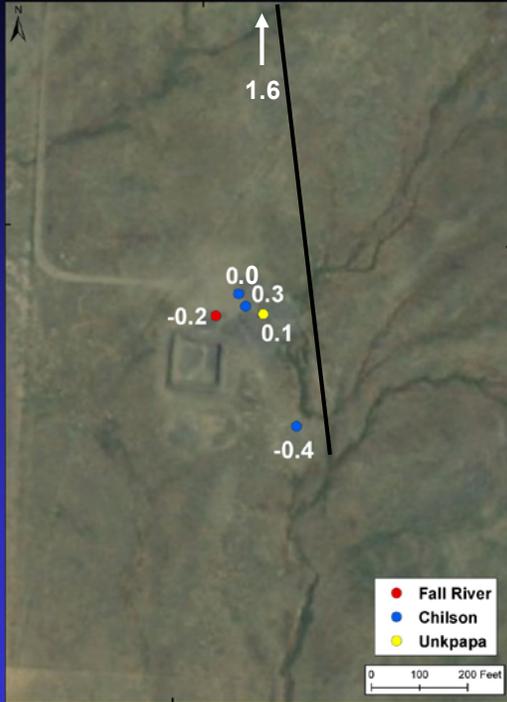
The rectangles indicate wells with some detectable tritium, but are close to the measurement error. With this and possible TVA contamination, an age greater or less than 60 years is uncertain.

All other wells have very low tritium values and the groundwaters in those wells are likely greater than 60 years old.

# Dewey Area Tritium (TU)



# Burdock Area Tritium (TU)



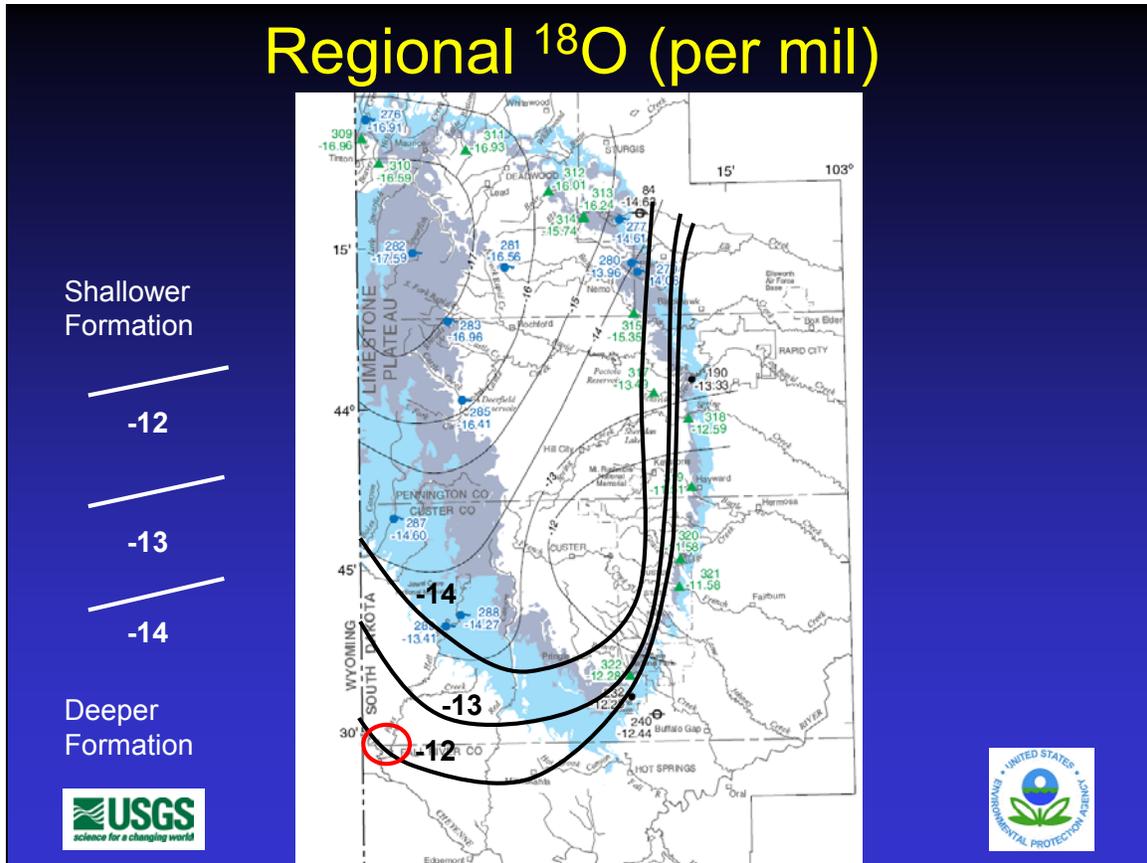
## $^{18}\text{O}$

- Naturally occurring stable water isotope
- Conservative tracer, not reactive
- More negative at higher altitude (or during a colder climate)
- Good tracer for recharge source
- Good tracer for evidence of aquifer connections
- Error (1 SD) of about +/- 0.06 per mil
- Do not have direct data for Pass Creek or local precipitation (both could vary throughout the year)



SD = standard deviation.

Not reactive indicates that the isotopic value does not change once recharge water becomes groundwater.



Data is from wells, springs, and stream flow.

Map is from Black Hills Regional Hydrology Study by the USGS, reference is:

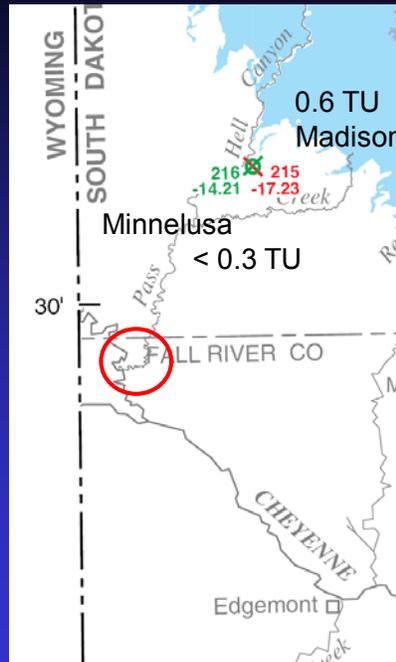
Naus, C.A., Driscoll, D.G., and Carter, J.M., 2001, Geochemistry of the Madison and Minnelusa aquifer in the Black Hills area, South Dakota: U.S. Geological Survey, Water-Resources Investigations Report 01-4129, 118 p.

Black lines are a re-interpretation of the isotope contour lines based more on elevation.

Red circle = site area.

Listing on the left is a conceptual diagram of how values should be more negative with depth, if recharge occurs at the unit outcrop.

## Local $^{18}\text{O}$ (per mil)

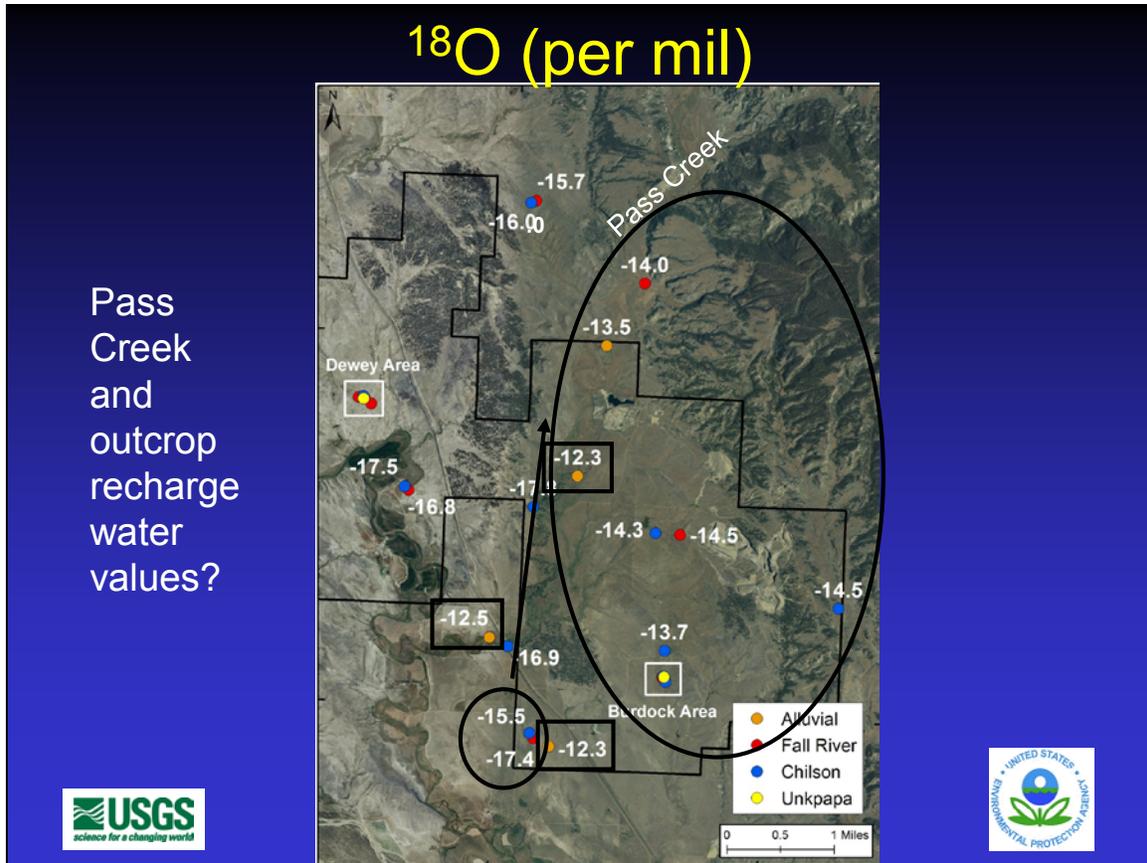


Red circle = site area.

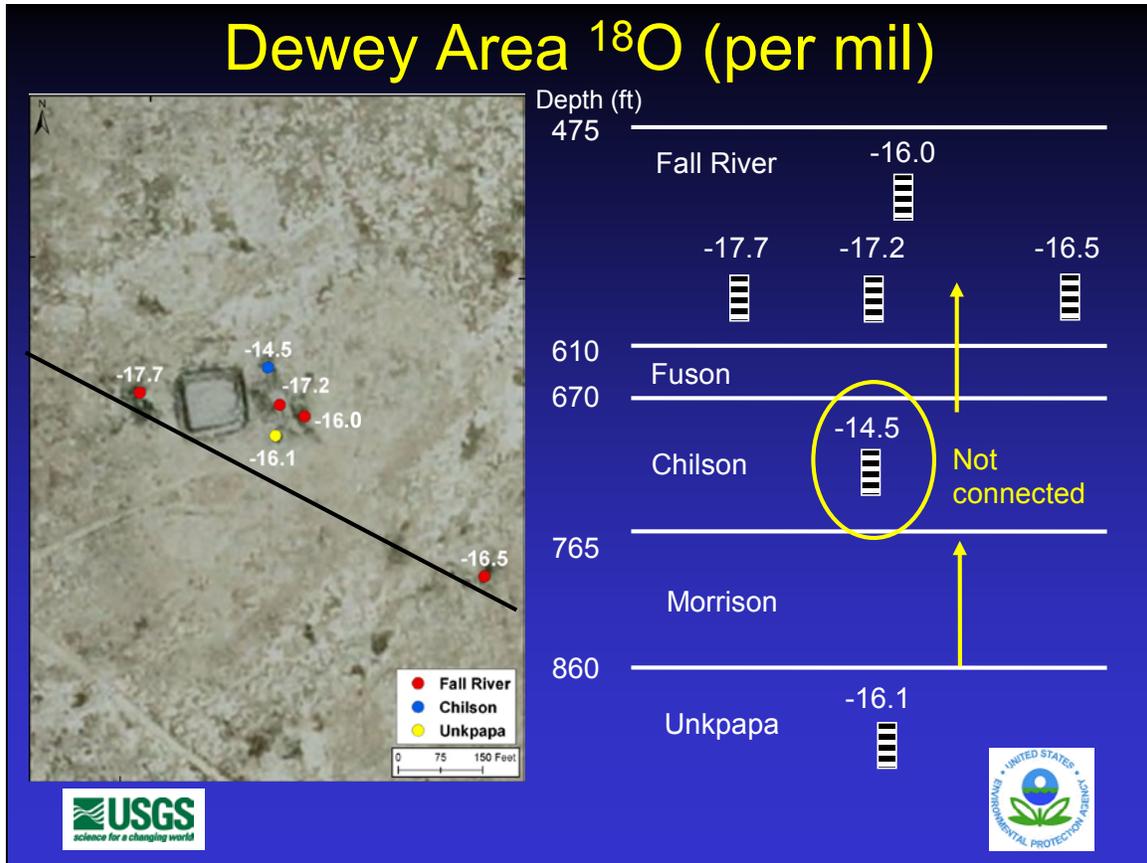
The Madison is a deep karstic limestone (below the Minnelusa) and is presumably recharged at higher elevation (thus lower oxygen isotope value). Karstic nature may allow for fast transport of groundwater, thus the 0.6 TU value for tritium.

Map is modified from the Black Hills Regional Hydrology Study by the USGS, reference is:

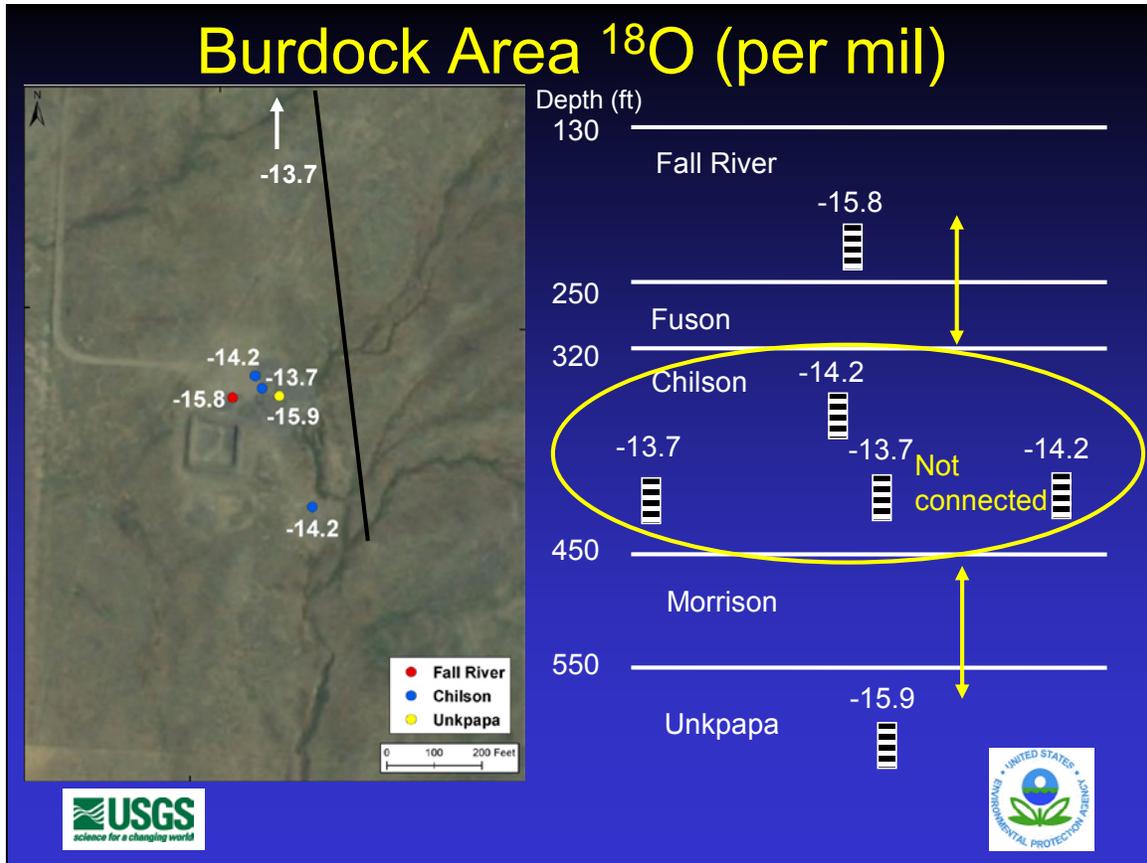
Naus, C.A., Driscoll, D.G., and Carter, J.M., 2001, Geochemistry of the Madison and Minnelusa aquifer in the Black Hills area, South Dakota: U.S. Geological Survey, Water-Resources Investigations Report 01-4129, 118 p.



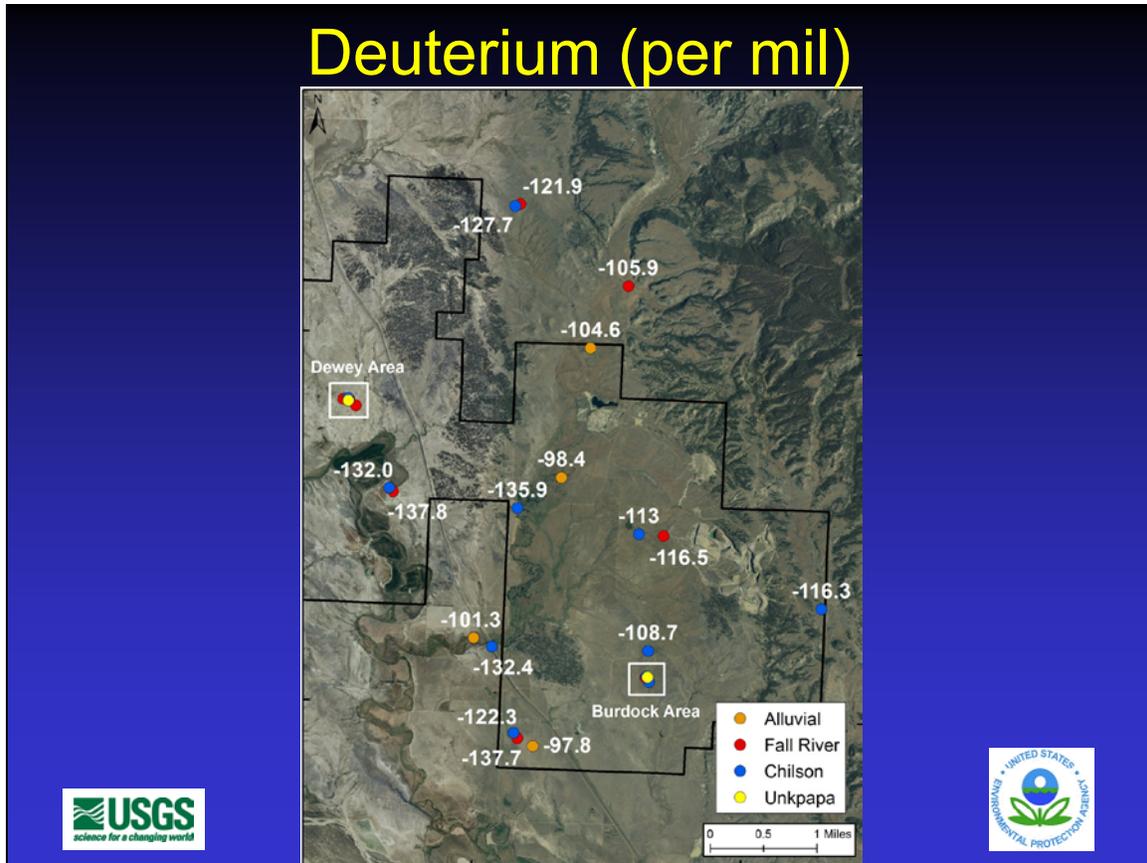
Samples for local precipitation and local streams are not available. Rectangles indicate alluvial wells that are likely recharged locally ( $^{18}\text{O}$  near -12), which makes sense based on slide #15. Any values that are more negative are probably groundwater that is not derived from local recharge (although precipitation values at the initial Black Hills uplift on the right side of the slide are unknown). Large circle indicates the Burdock area in general has similar oxygen isotope values, but the two downgradient wells (-15.5 and -17.4 in the smaller circle) appear to be groundwaters with a different source (more similar to Dewey area waters). The long arrow indicates that these more negative values may be derived from stream flow loss out of Pass Creek.



This area has upward hydraulic heads (40 ft. higher in the Chilson than the Fall River); however, oxygen isotopes do not indicate a strong transfer of water across the local aquitards (Fuson and Morrison), albeit only one sample is available in the Chilson.

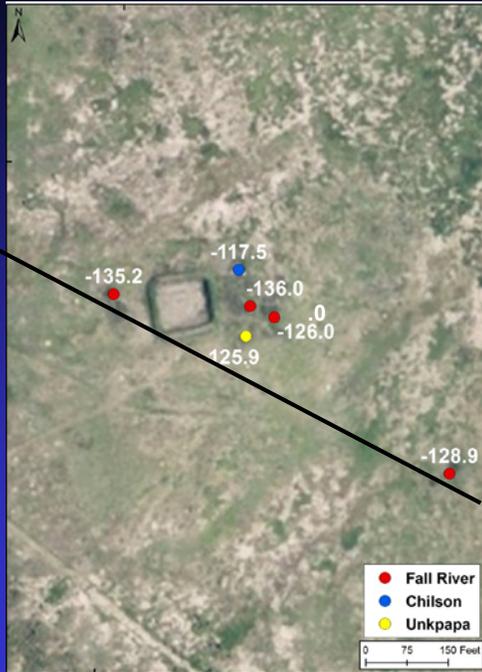


Double arrows indicate that there is no significant hydraulic head across the units. Oxygen isotopes do not indicate a strong transfer of water across the local aquitards (Fuson and Morrison).



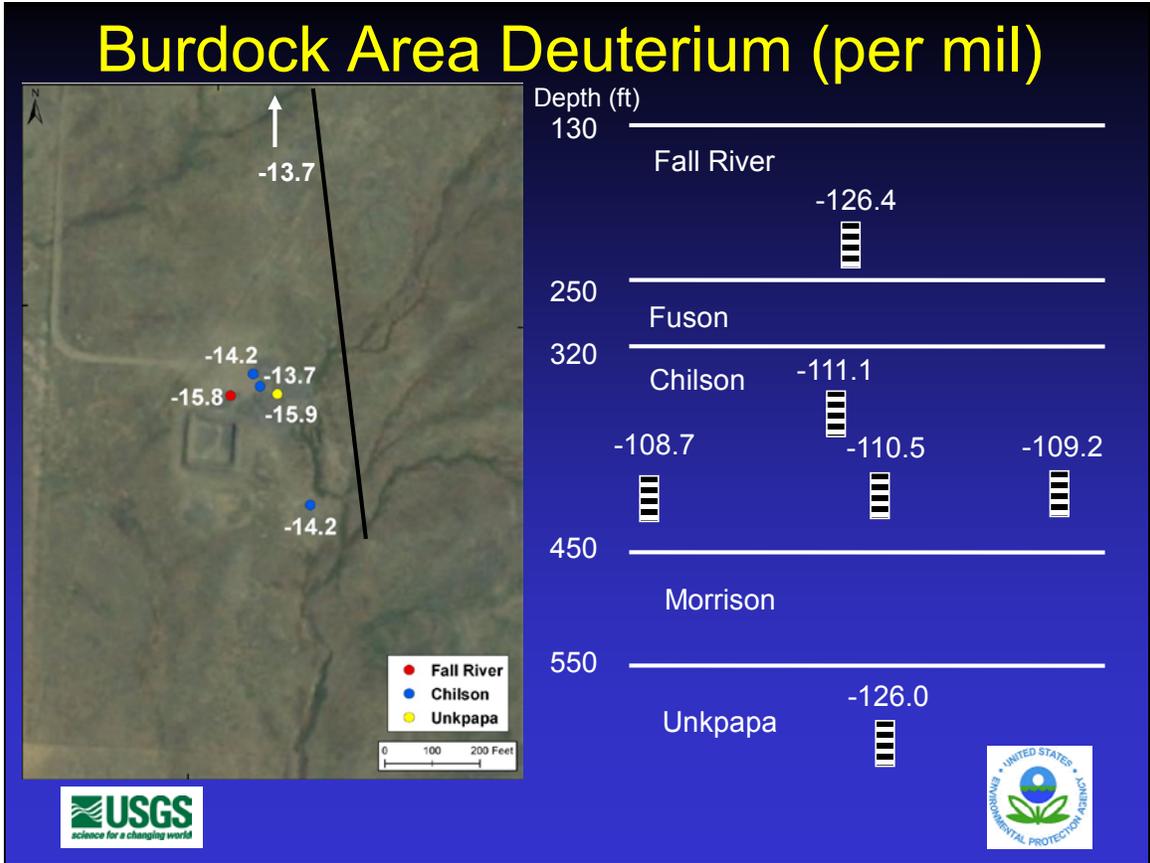
$^{18}\text{O}$  and deuterium are measured on the same sample. Deuterium data show similar information and trends as  $^{18}\text{O}$ .

# Dewey Area Deuterium (per mil)



Depth (ft)	Location	Deuterium (per mil)
475	Fall River	-126.0
		-135.2
		-128.9
610	Fuson	-136.0
		-117.5
670	Chilson	-117.5
		-126.0
765	Morrison	-126.0
		-128.9
860	Unkpapa	-125.9
		-126.0

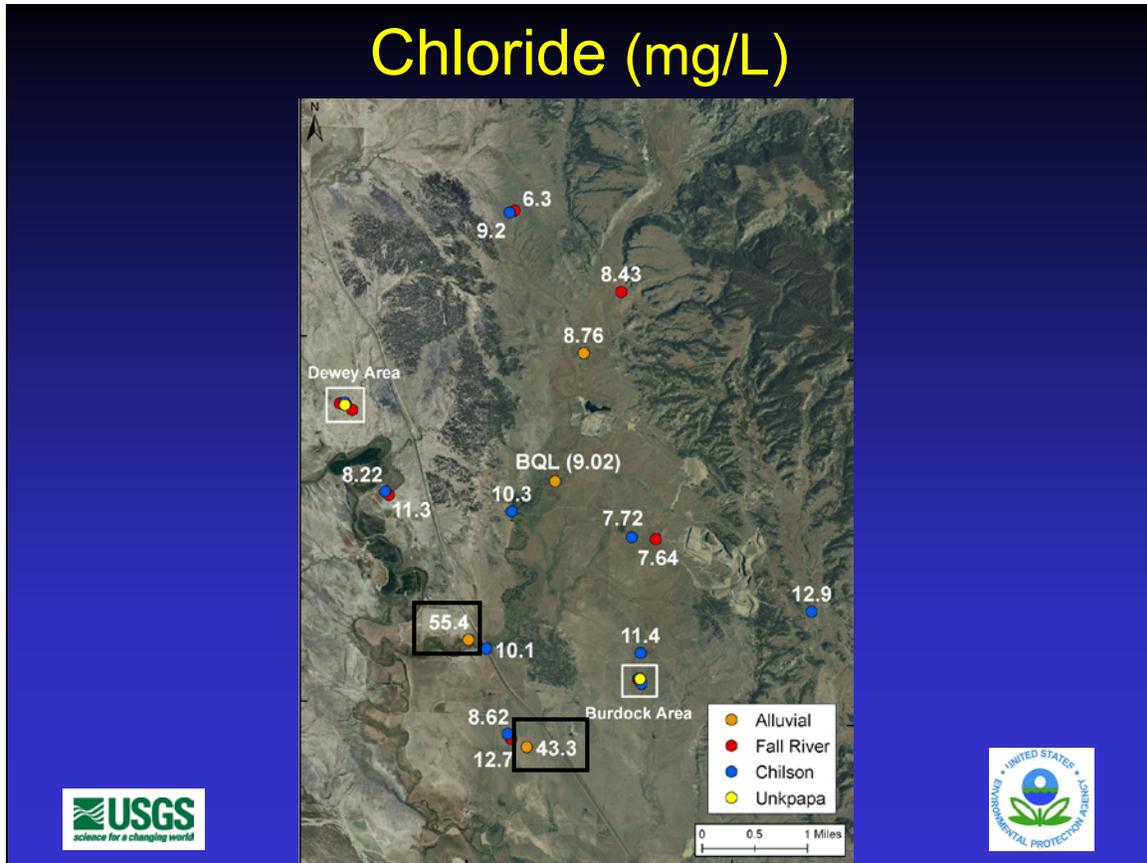




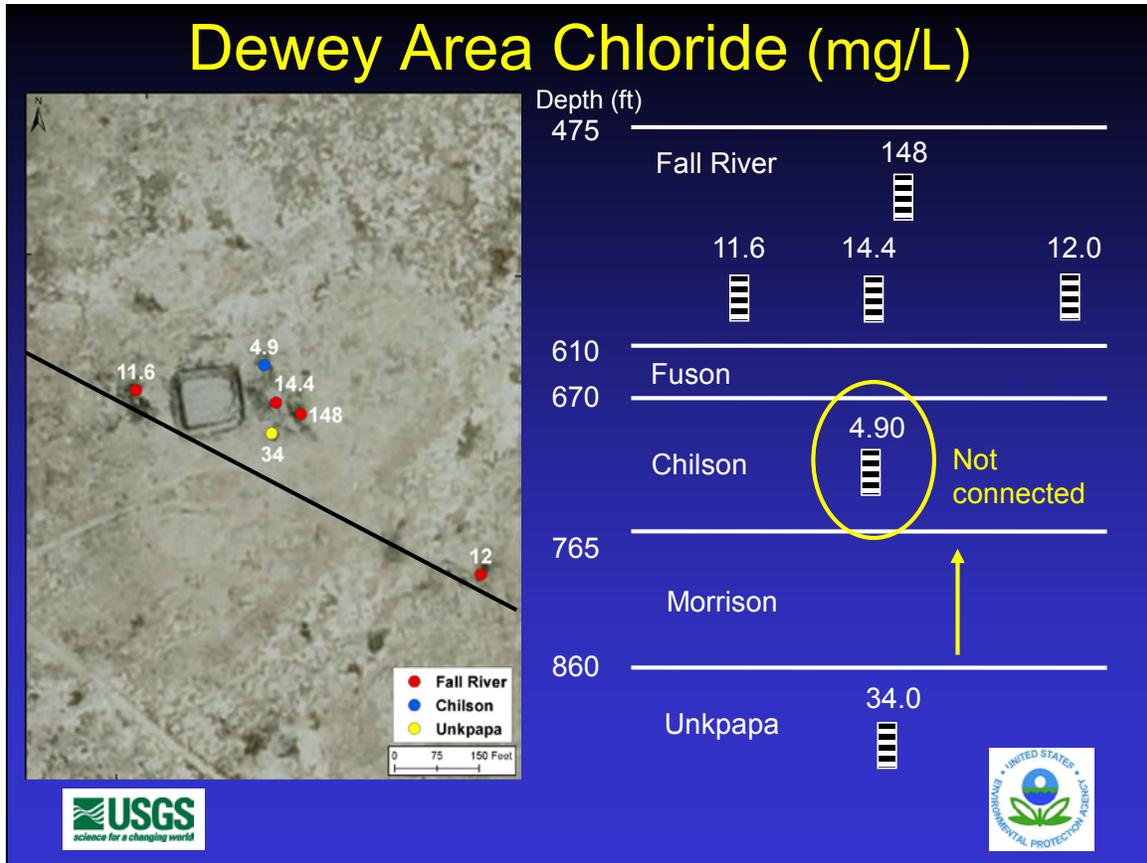
# Chloride

- Conservative tracer
- Dissolution of salt (NaCl)
- May increase along a flow path, but should not decrease
- Good tracer for evidence of aquifer connections
- Detection limit of 1.0 mg/L

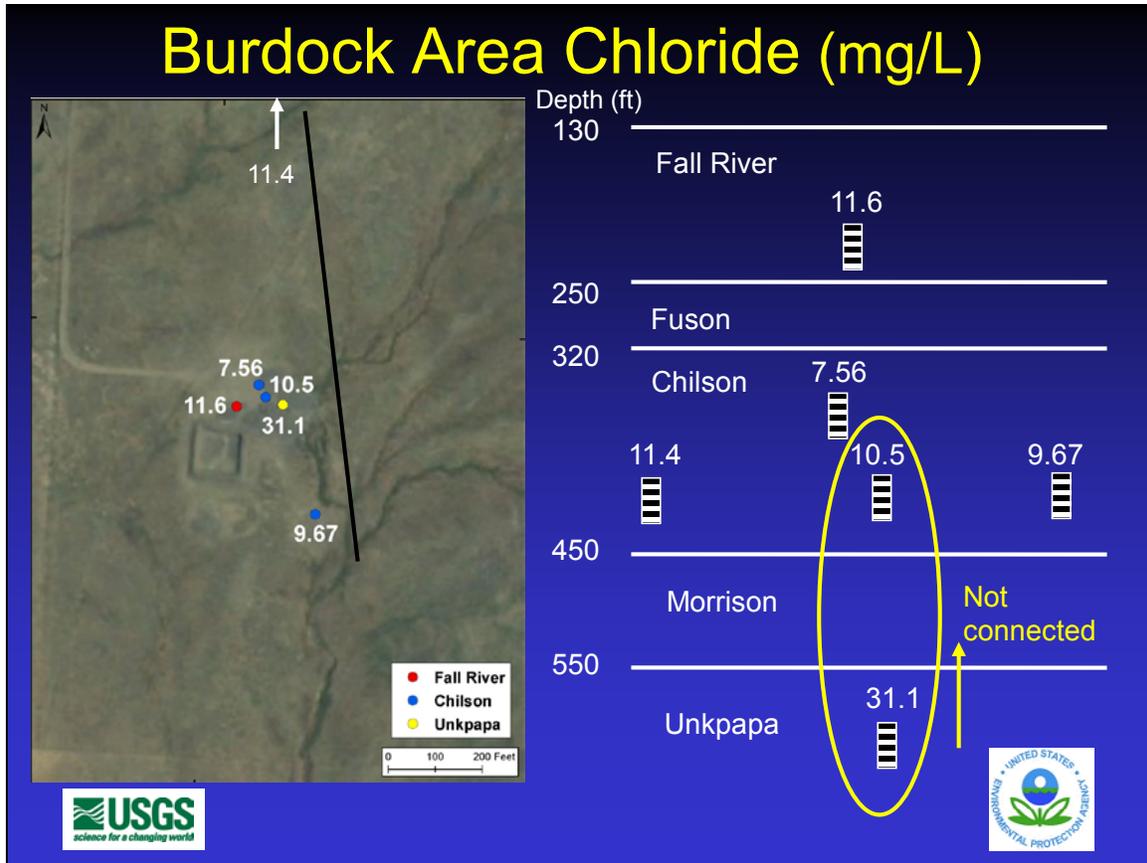




Black rectangles indicate alluvial aquifer wells that probably contact shales that have a higher chloride content.



If groundwater flow was significant in the upward direction, chloride would not decrease.



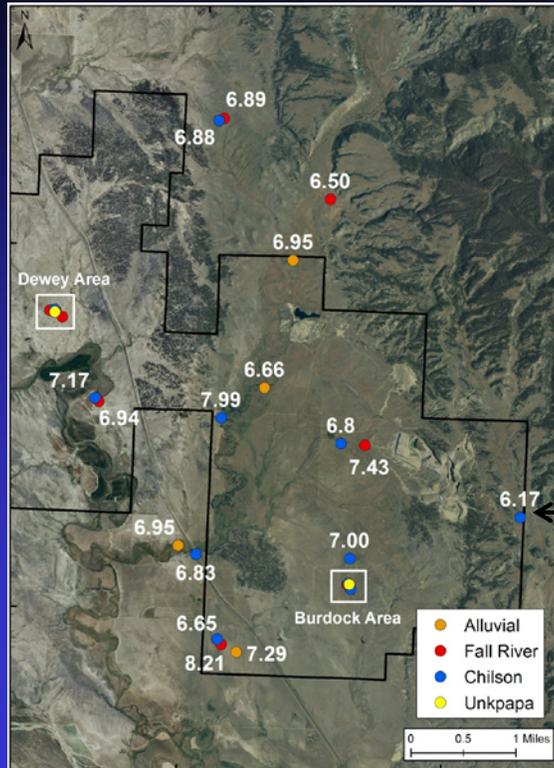
If groundwater flow was significant in the upward direction, chloride would not decrease.

## pH

- Generally near neutral
- High pH in Unkpapa wells, have lower carbon dioxide concentrations (degasses along the flow path?, this would increase the pH value)
- Lower pH at well 3026 where active sulfide oxidation is occurring



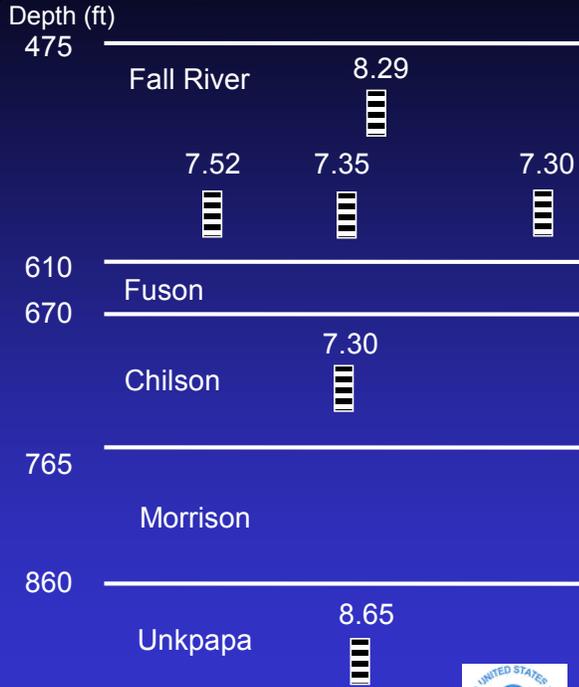
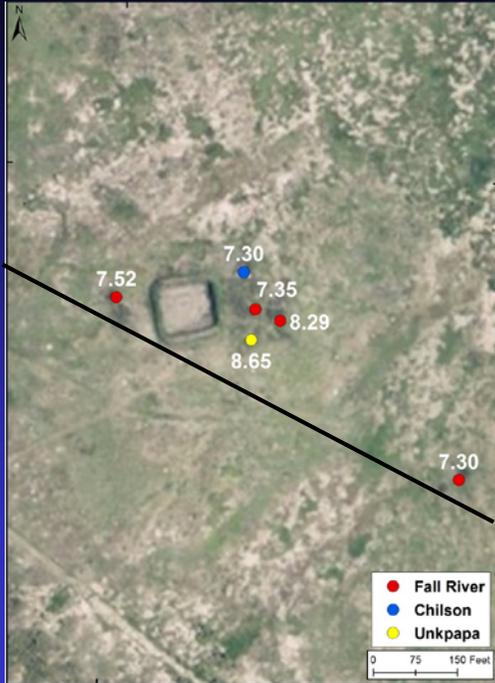
# pH



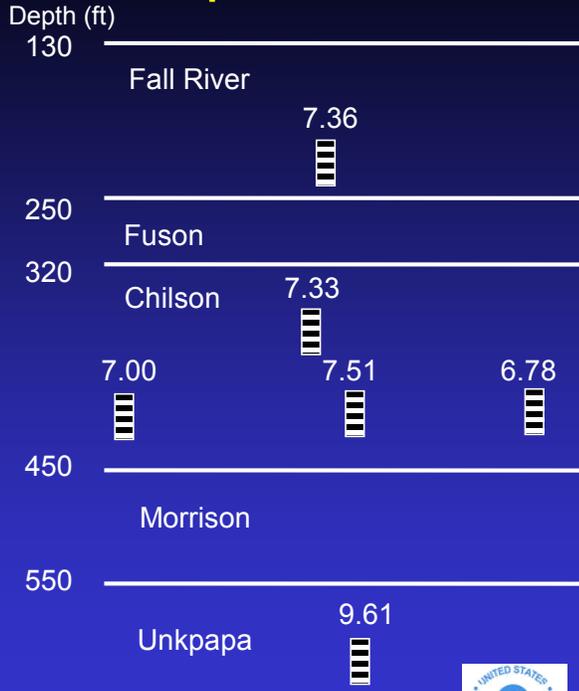
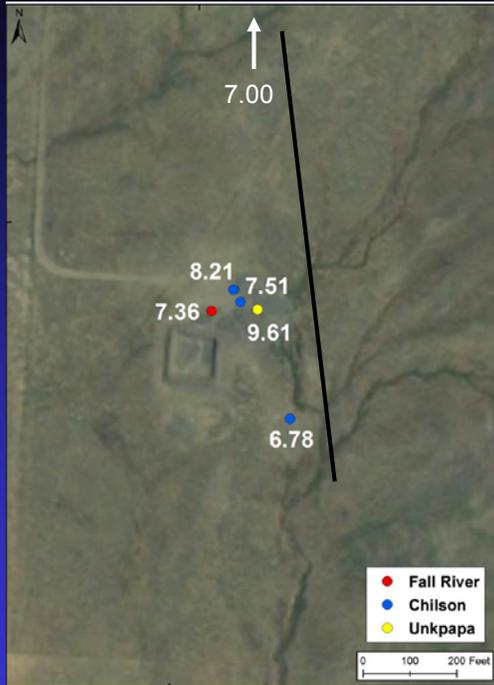
Well 3026



# Dewey Area pH



# Burdock Area pH

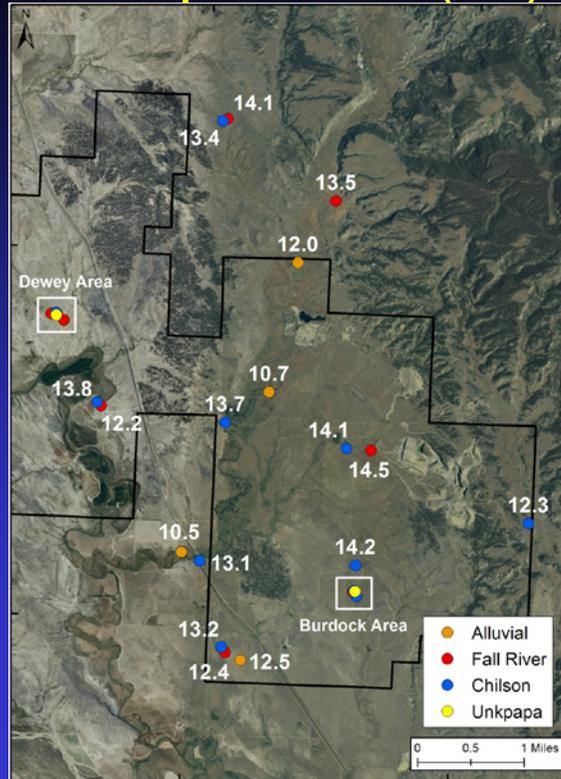


# Temperature

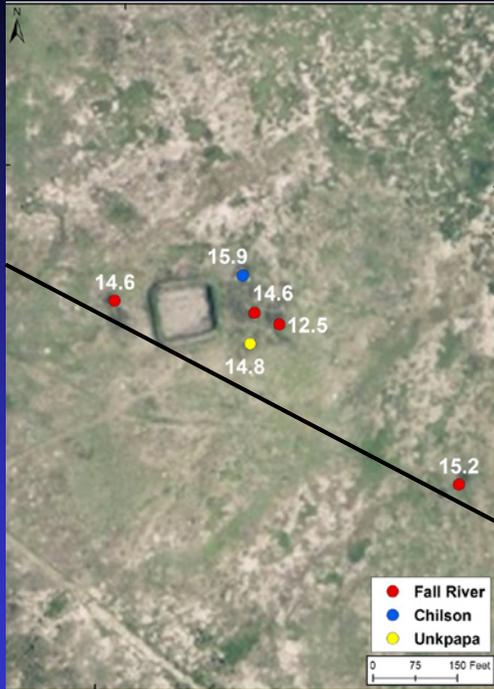
- Included for reference
- Shallow wells appear to have slightly colder temperature (lag in June when sampling after winter?)
- Deeper wells have a relatively constant temperature



# Temperature (°C)

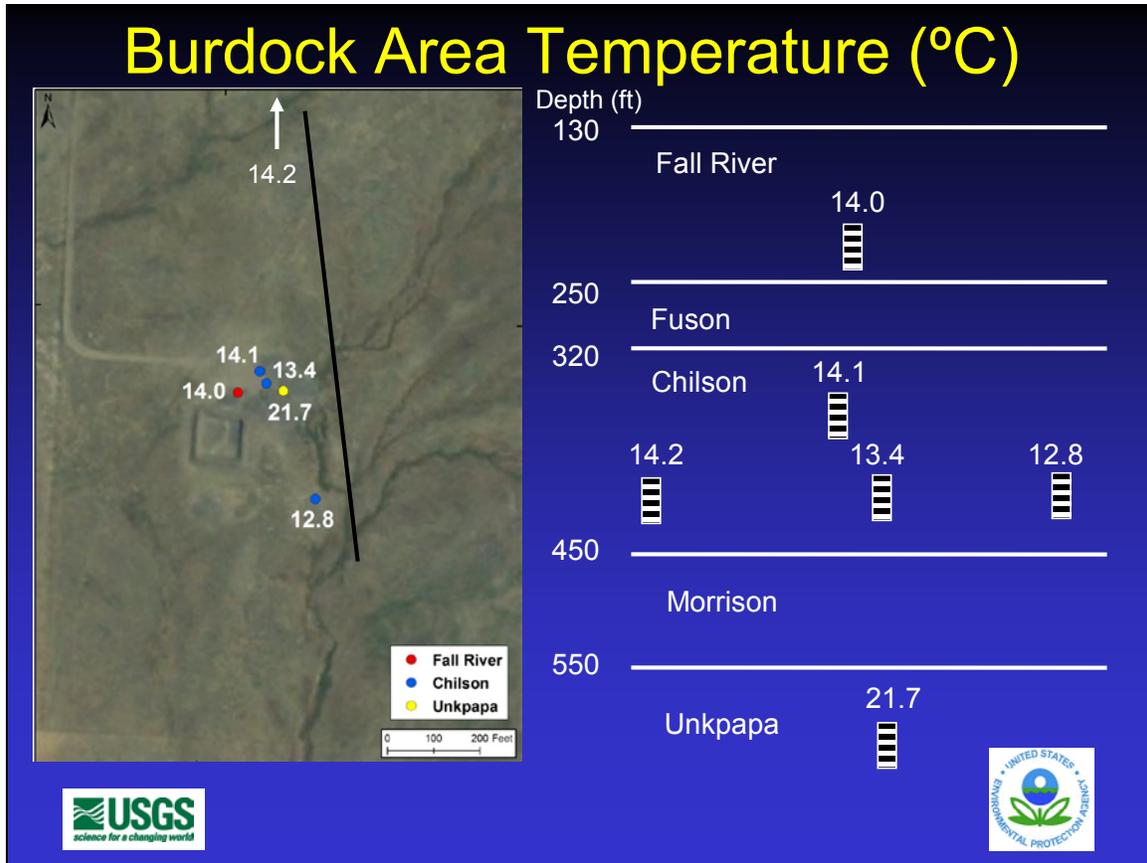


# Dewey Area Temperature (°C)



Depth (ft)	Temperature (°C)
475	12.5
610	14.6, 14.6, 15.2
670	15.9
765	
860	14.8





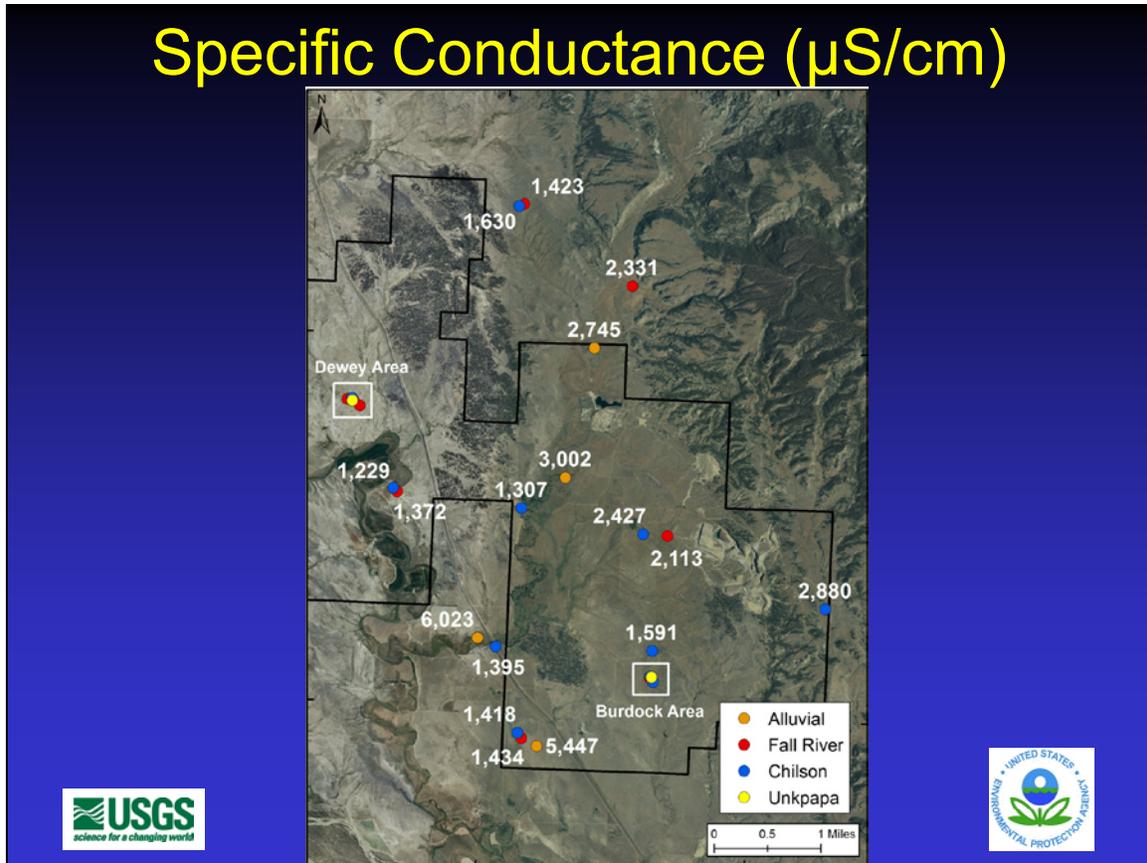
Unkpapa well was very slow flowing and water probably warmed up in the sample tubing.

## Specific Conductance

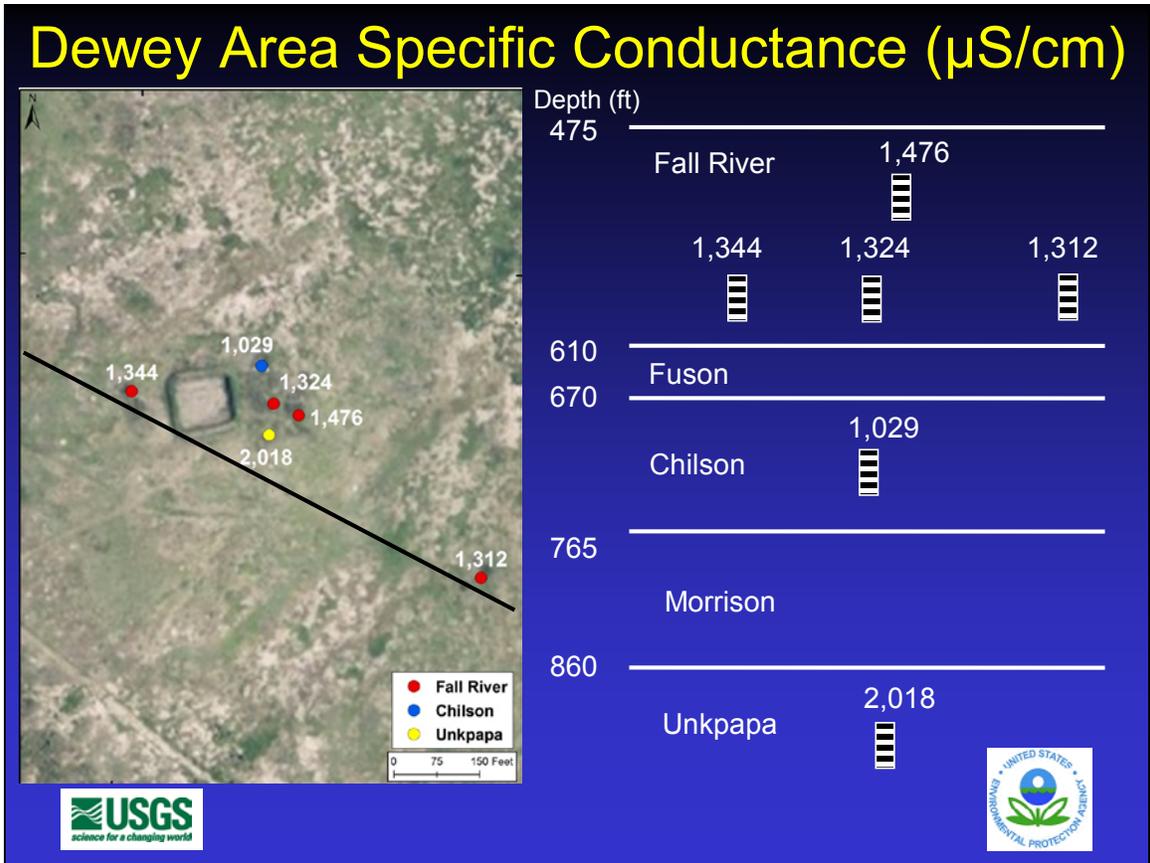
- Easily measured with a handheld meter
- Indicates overall concentration of dissolved constituents
- Does not indicate any particular constituent

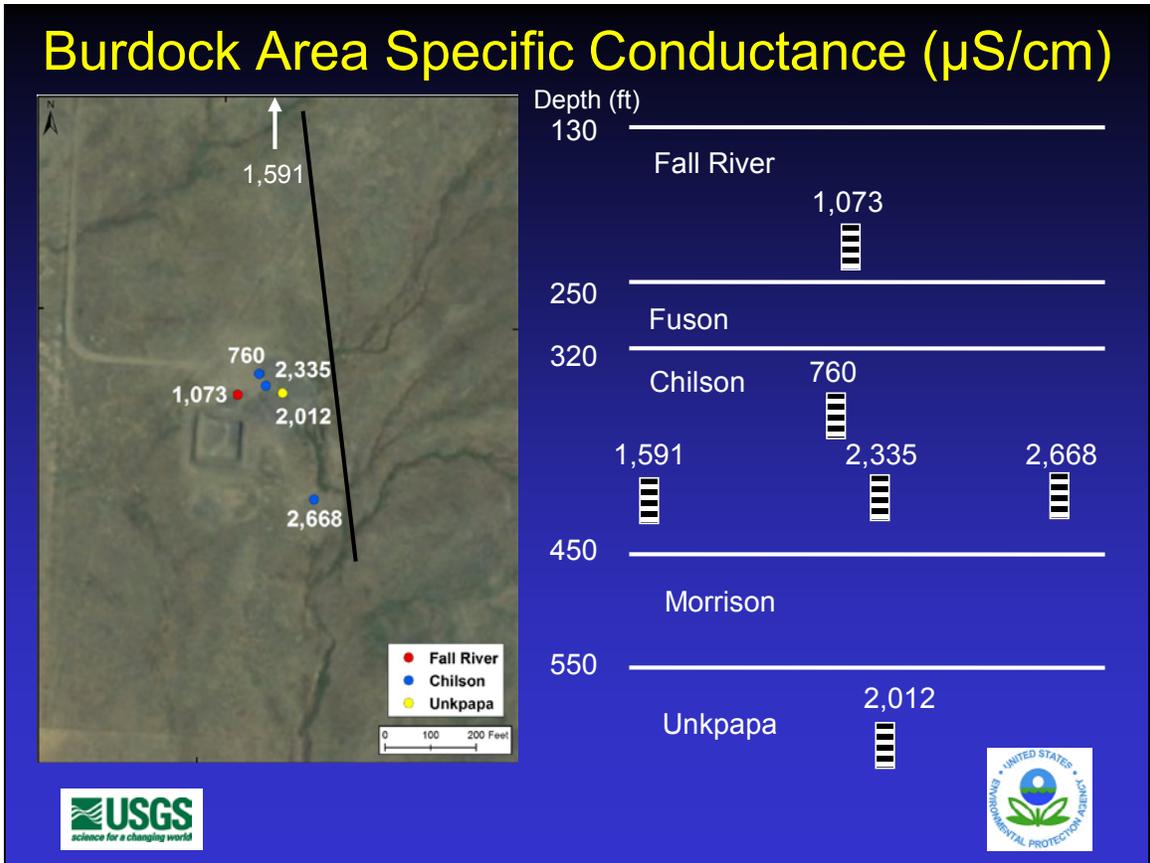


## Specific Conductance ( $\mu\text{S}/\text{cm}$ )



Overall, higher specific conductance in shallow alluvial wells that contact or are near underlying shales.



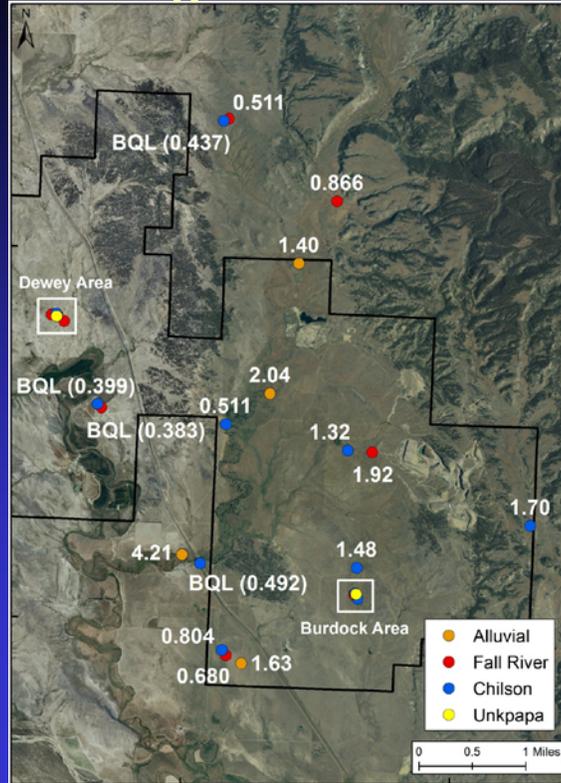


## Dissolved Organic Carbon (DOC)

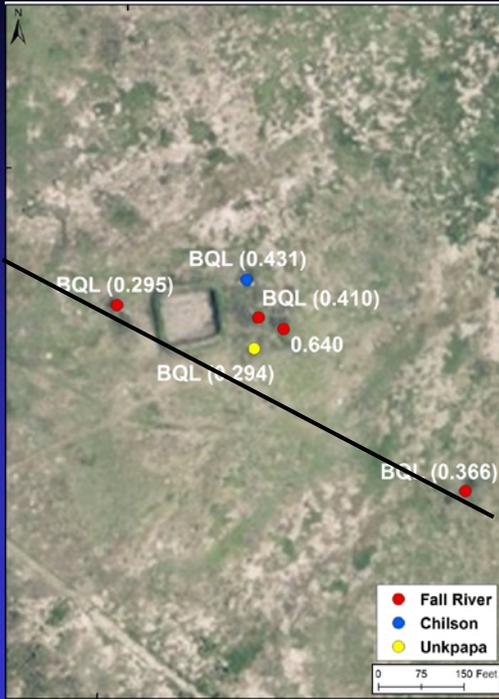
- Difficult to get blank samples much less than 0.2-0.5 mg/L
- High DOC could indicate a lot of organic material in the solid phase
- High DOC could indicate a greater reducing capacity of the groundwater (no dissolved oxygen present)



# Dissolved Organic Carbon (mg/L)

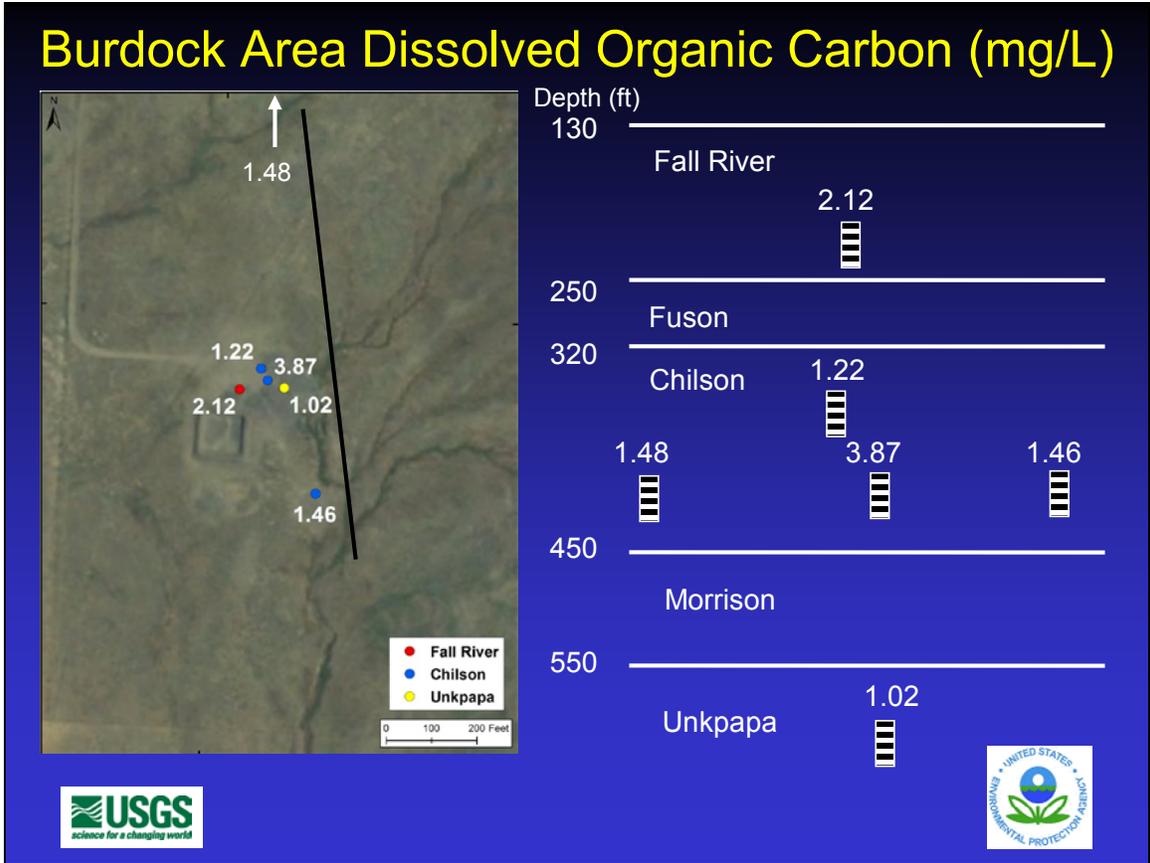


# Dewey Area Dissolved Organic Carbon (mg/L)



Depth (ft)	Location	DOC (mg/L)
475	Fall River	0.640
		0.295, 0.410, 0.366
610	Fuson	
670	Chilson	0.431
765	Morrison	
860	Unkpapa	0.294

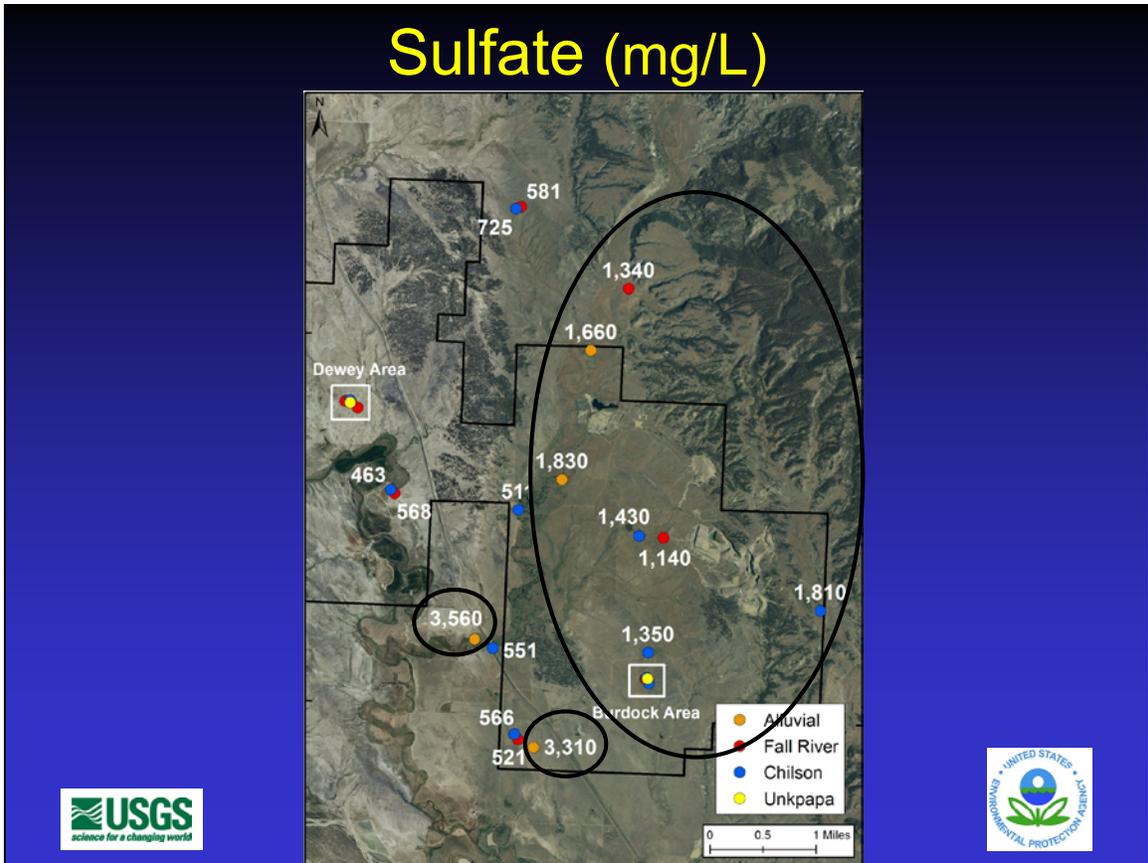




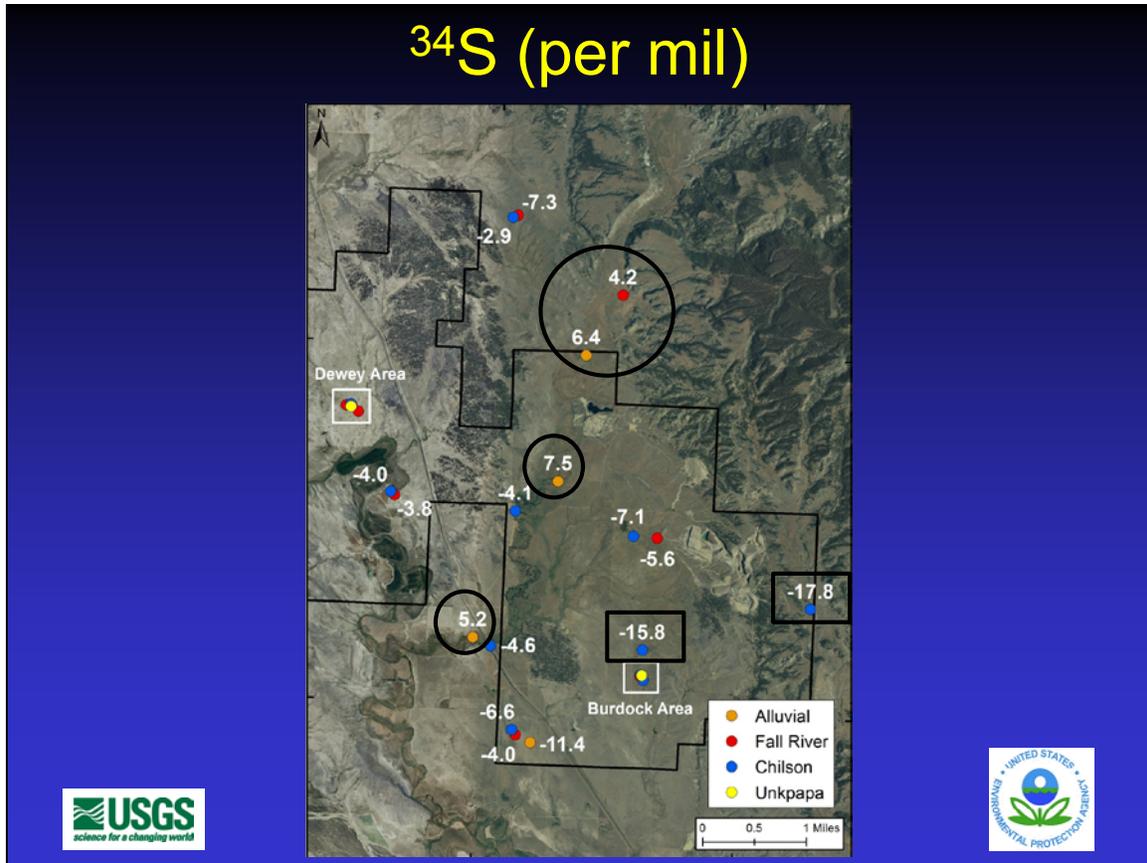
## $^{34}\text{S}$ and Sulfate

- Sulfur is in solution as sulfate
- Sulfate source is either
  - Gypsum or anhydrite ( $\text{CaSO}_4$ ) – positive  $^{34}\text{S}$  value
  - Sulfide oxidation – negative  $^{34}\text{S}$  value
- Intermediate  $^{34}\text{S}$  values = mixed source
- Dewey area – some additional sulfate dissolution is possible (slightly undersaturated for gypsum)
- Burdock area – near gypsum saturation, sulfate is relatively non-reactive
- If anything, sulfate would tend to increase along a flow path (no evidence of sulfate reducing groundwaters which would precipitate sulfides)
- Error (1 SD) of about +/- 0.15 for  $^{34}\text{S}$  and detection limit for sulfate of 1 mg/L

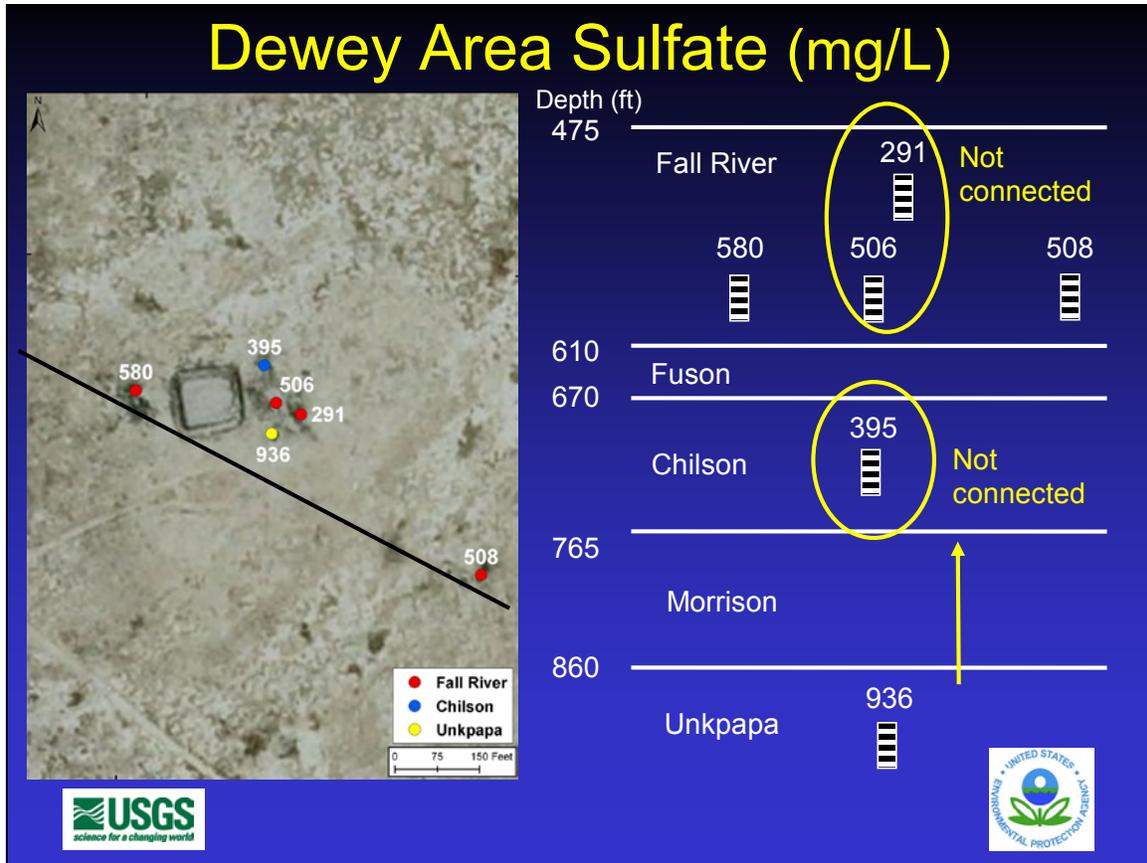




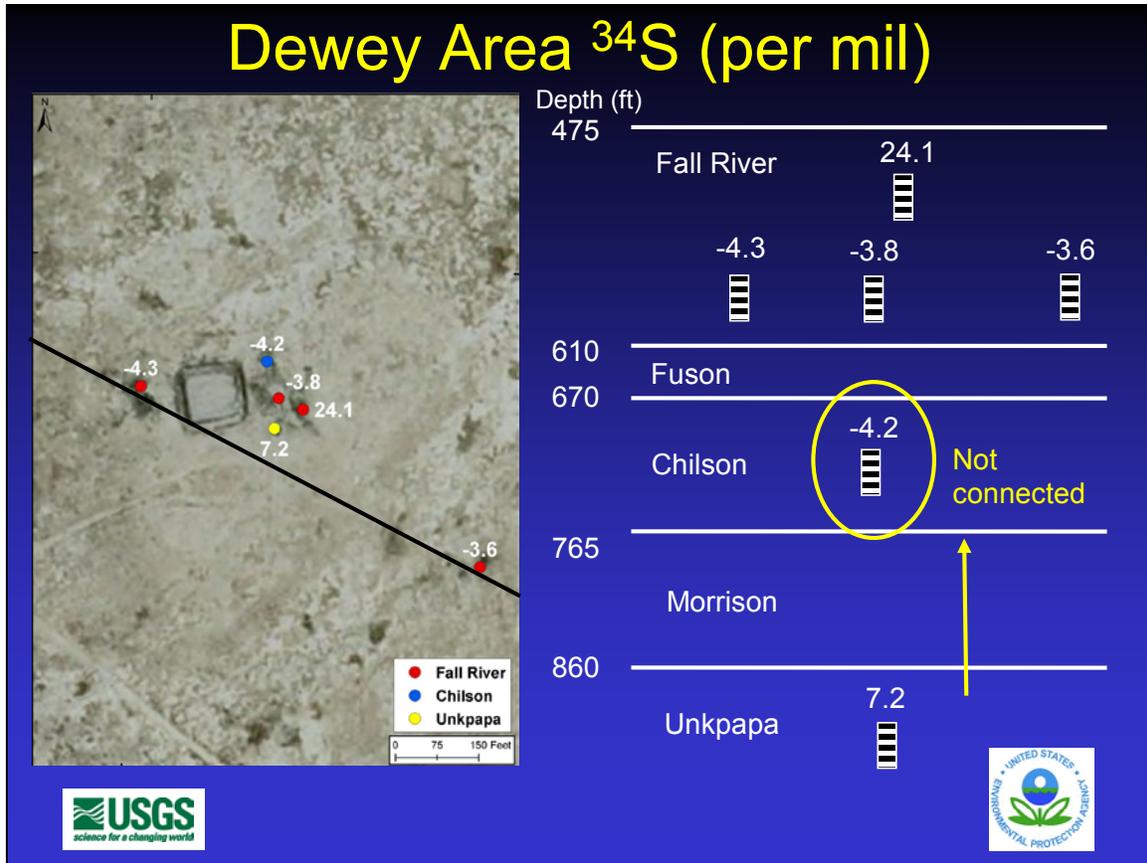
Large circle indicates Burdock area with sulfate near 1,500 mg/L. Small circles indicate alluvial wells near shale bedrock and resulting high sulfate concentration. Wells outside of the Burdock area are all near 500-700 mg/L sulfate.



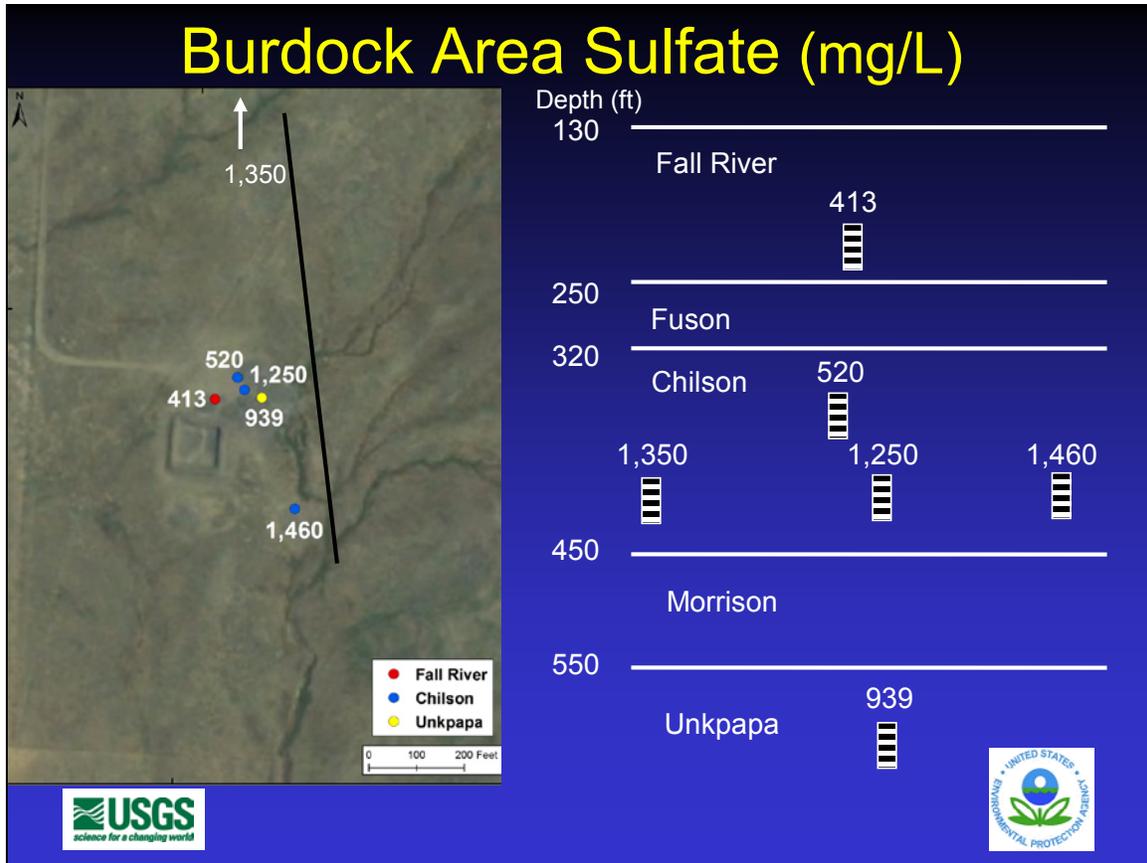
Rectangles indicate wells with more negative values due to sulfide oxidation.  
Circles indicate wells with more positive values indicative of gypsum dissolution.  
Intermediate values are likely due to mixing.

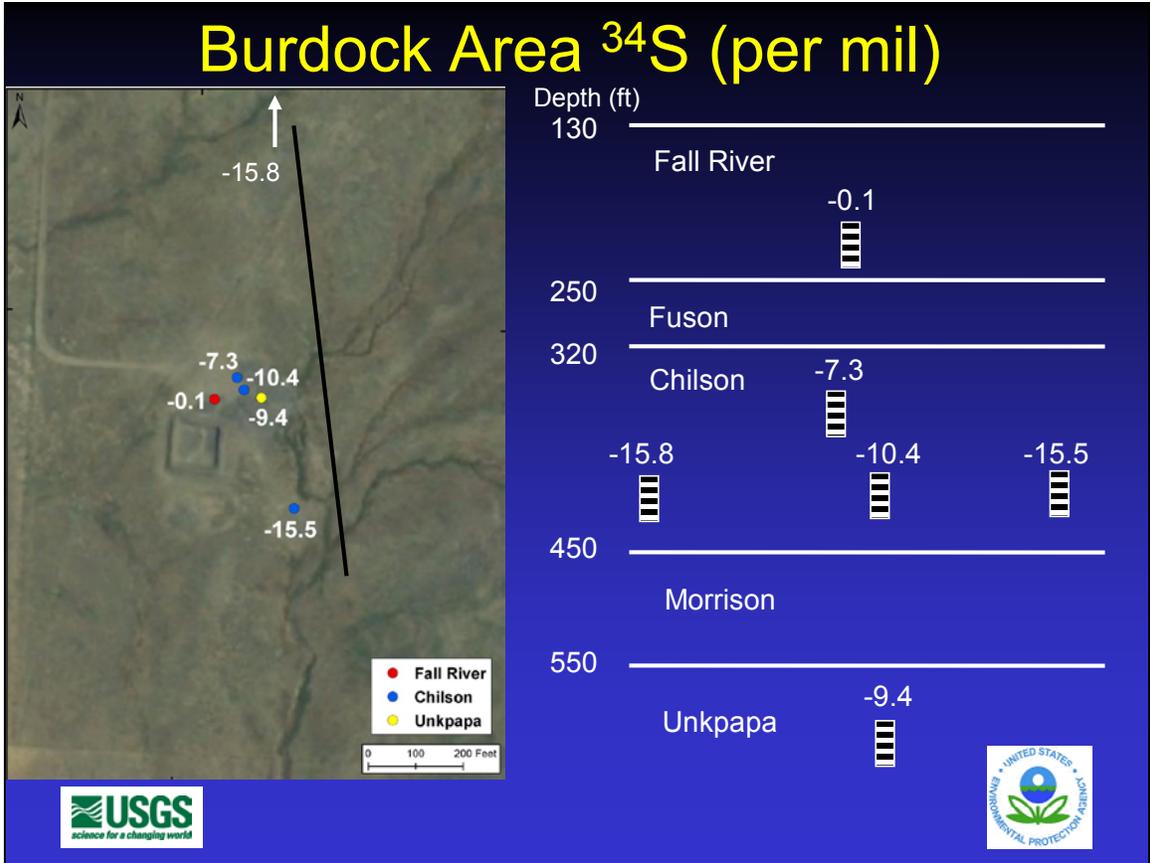


Groundwater connections do not appear likely, as sulfate concentration should only increase with more gypsum dissolution. Groundwater conditions are not known to be sulfate reducing (which would remove sulfate).



Groundwater connections do not appear likely, as sulfur isotopes are dramatically different and the Unkpapa does not have any oxygen that would cause sulfide oxidation and the production of more negative isotope values.

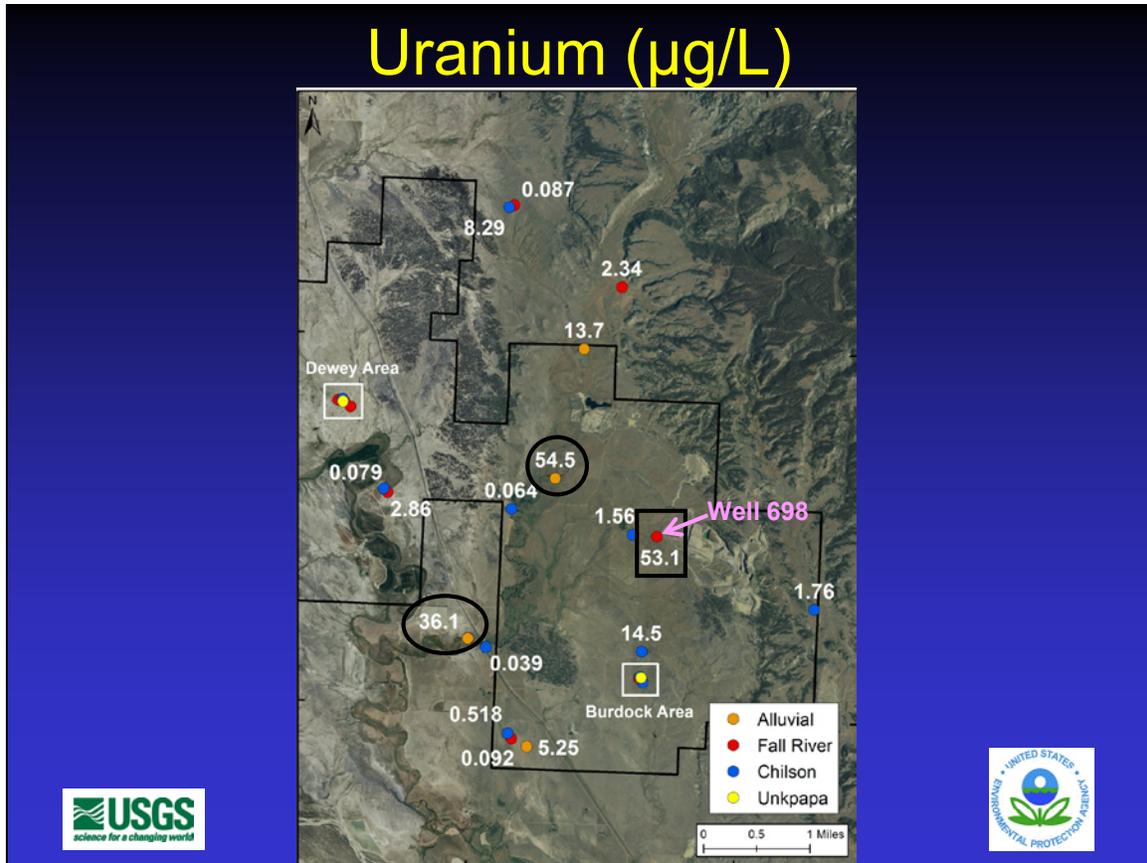




## Uranium

- Uranium is more soluble with oxidizing groundwater
- Uranium concentrations in deep units are all below drinking water standards (reducing conditions)
- Highest uranium is in alluvial wells
- Well 698 suggests that in order to precipitate uranium, contact with reductive solids is necessary beyond having no dissolved oxygen
- Detection limit is 0.007  $\mu\text{g/L}$



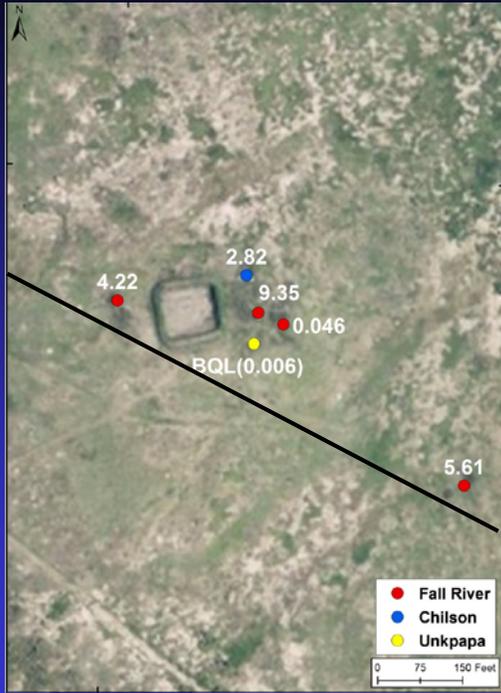


Circles indicate alluvial wells with higher uranium concentrations.

Well 698 (rectangle) does not have any DO, but does have iron and manganese, and solid-phase in that well is mostly oxidized.

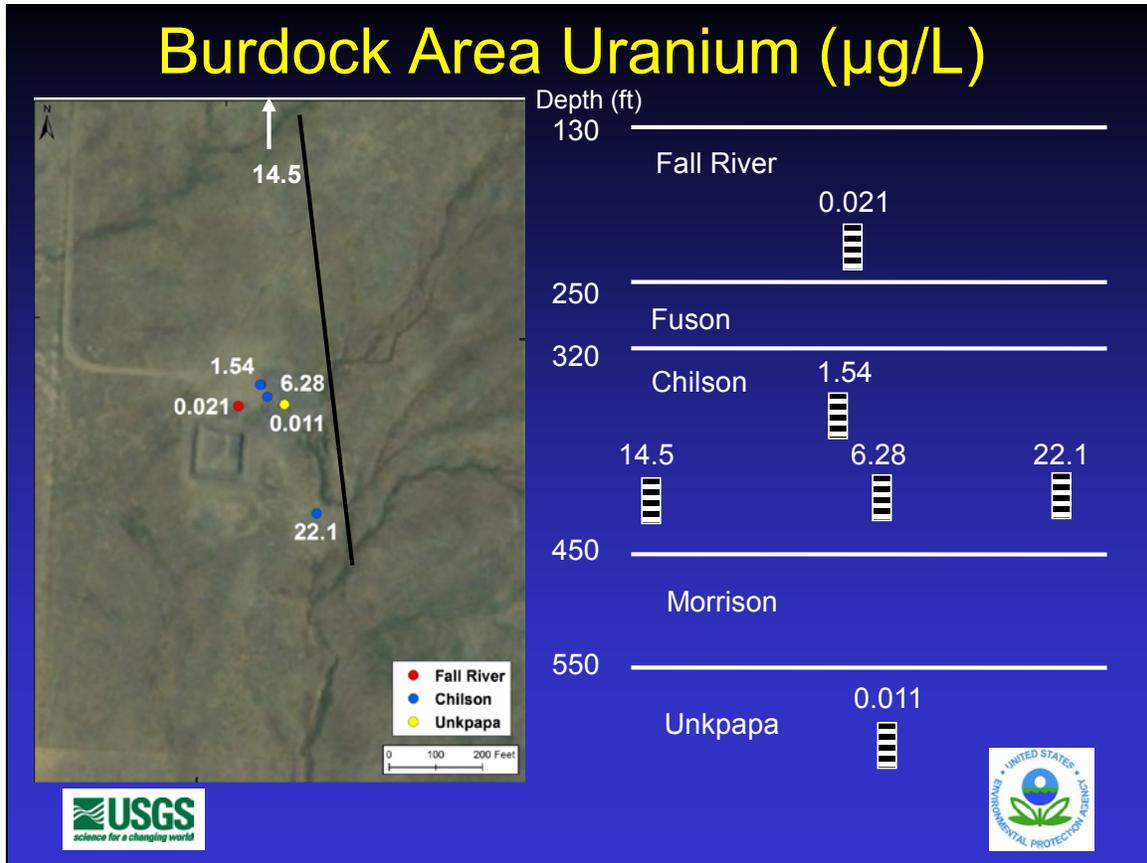
Well 698 is not necessarily water derived from a nearby open pit, since it does not have tritium. However, the Fall River Formation does have uranium in the solid phase, up gradient.

# Dewey Area Uranium ( $\mu\text{g/L}$ )



Depth (ft)	Location	Uranium ( $\mu\text{g/L}$ )
475	Fall River	0.046
		4.22
		9.35
610	Fuson	
		5.61
670	Chilson	2.82
765	Morrison	
860	Unkpapa	0.006





Wells 682 and 684 (14.5 and 22.1 ppb uranium) have some screening in the oxidized zone.

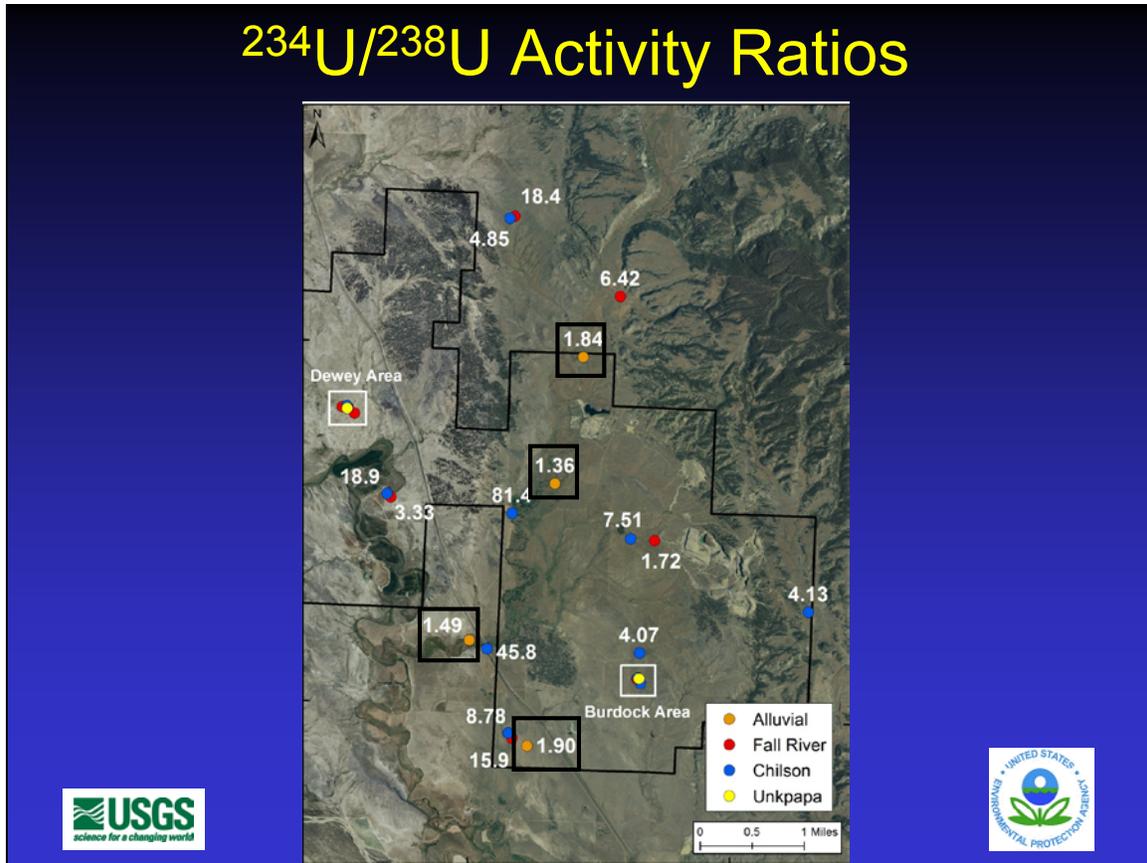
Well 680 (6.28 ppb) is all in the reducing zone.

## $^{234}\text{U}/^{238}\text{U}$ Activity Ratios

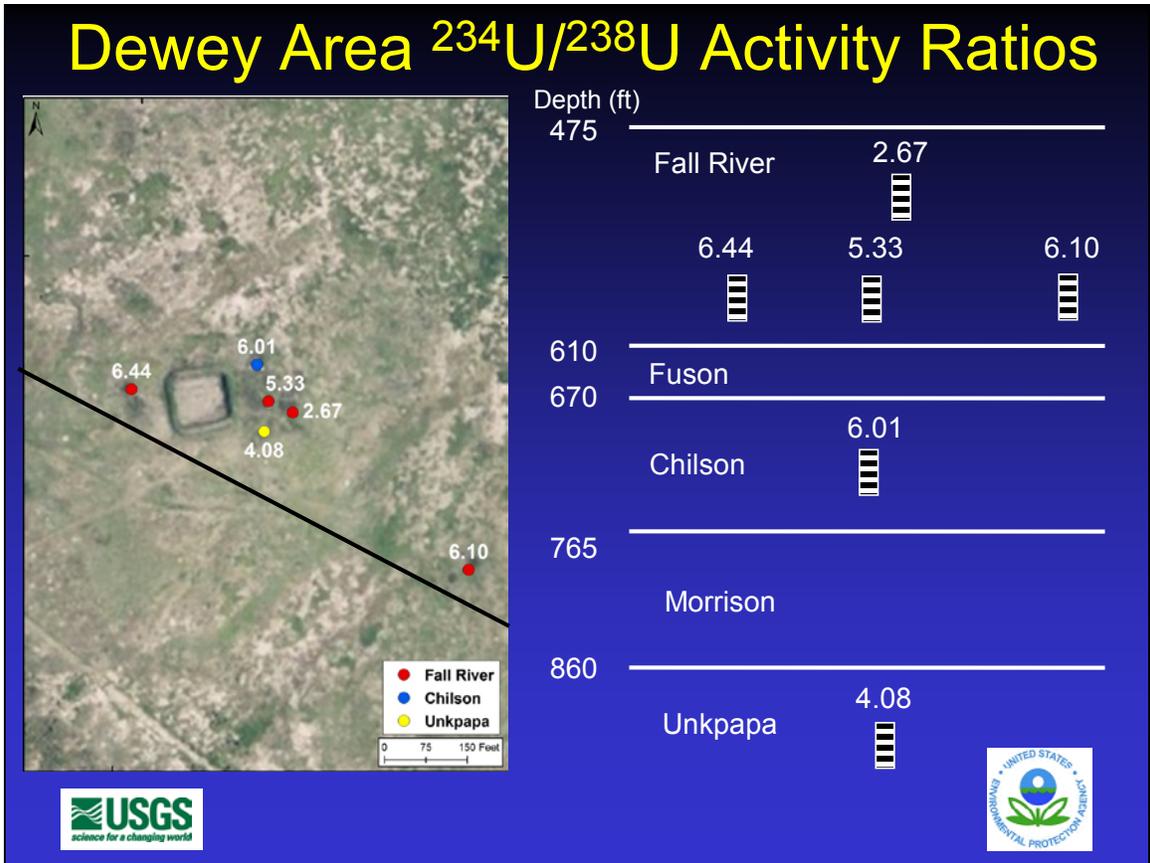
- $^{234}\text{U}$  leaches more readily than  $^{238}\text{U}$
- Higher ratios indicate a slower leaching process
- Values near 1.5 are typical of naturally occurring, young groundwaters

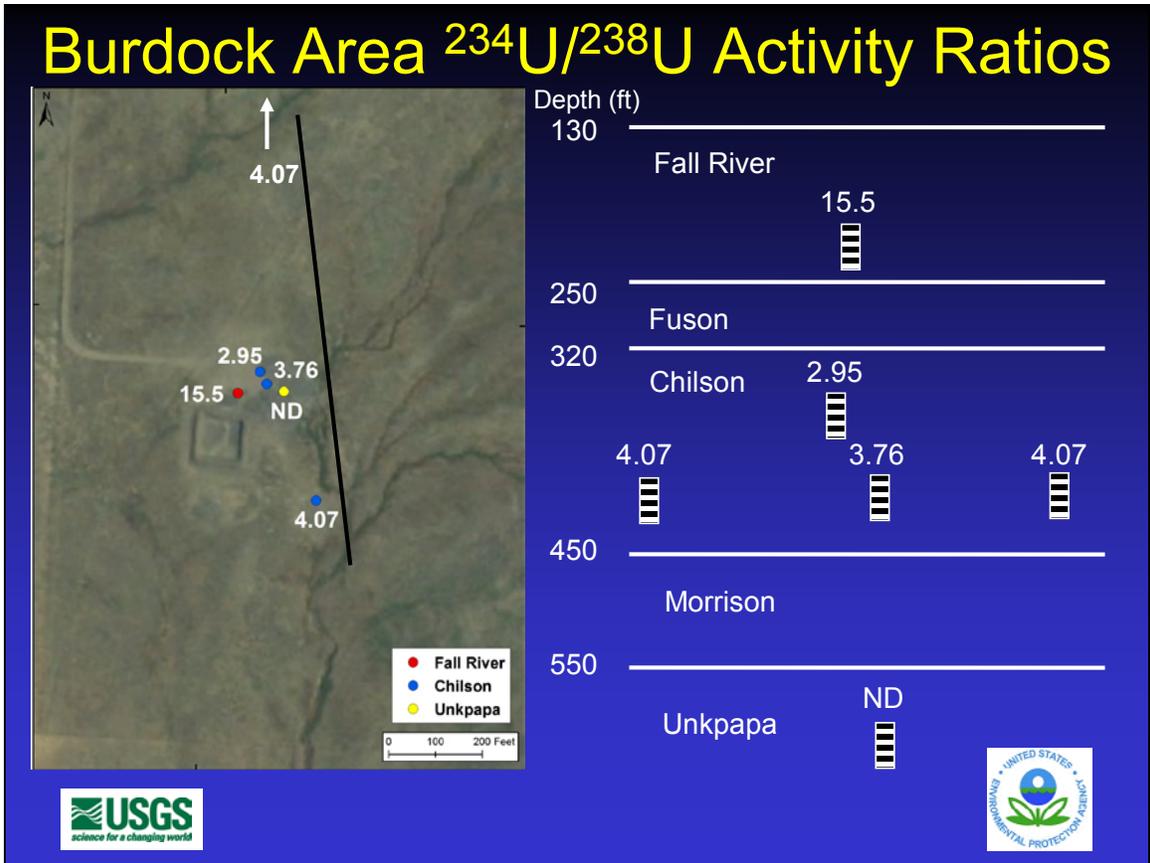


## $^{234}\text{U}/^{238}\text{U}$ Activity Ratios



Rectangles indicate alluvial wells with activity ratios typically found in groundwater. Many of the wells have much higher ratios, indicative of slow leaching of uranium from the solid phase.

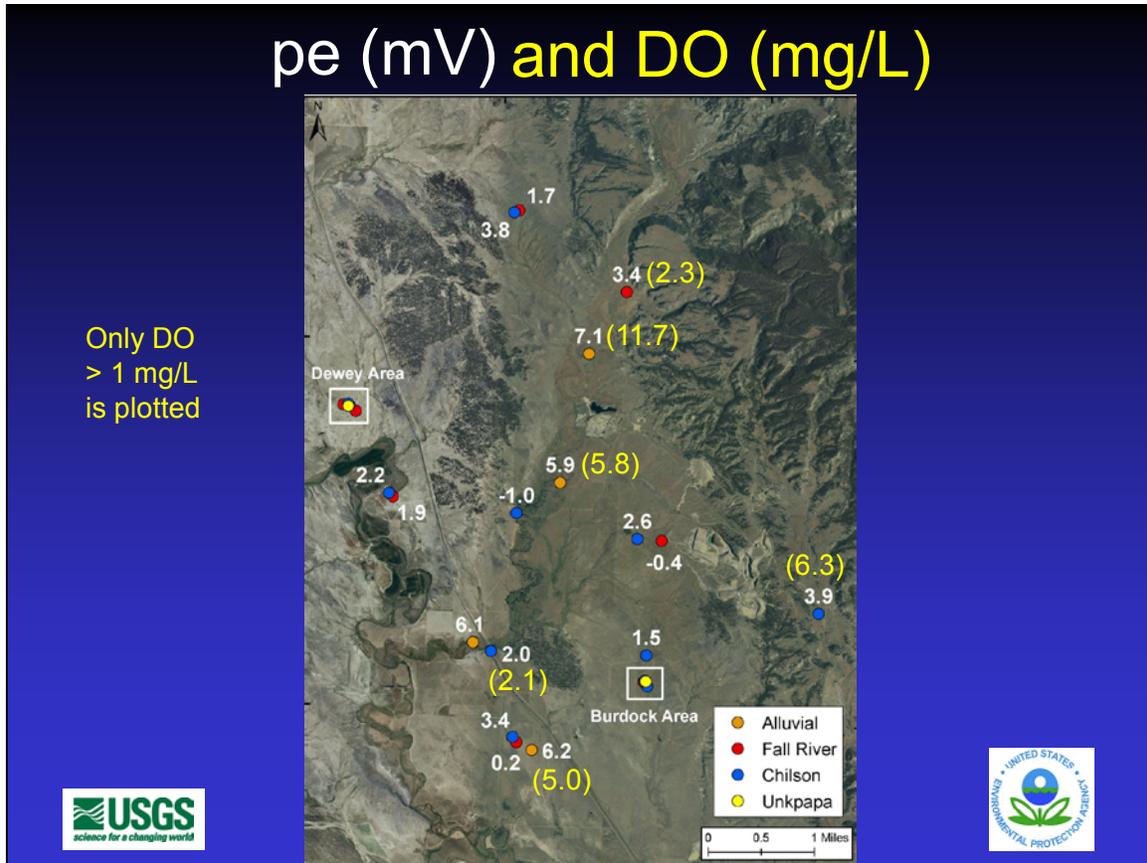




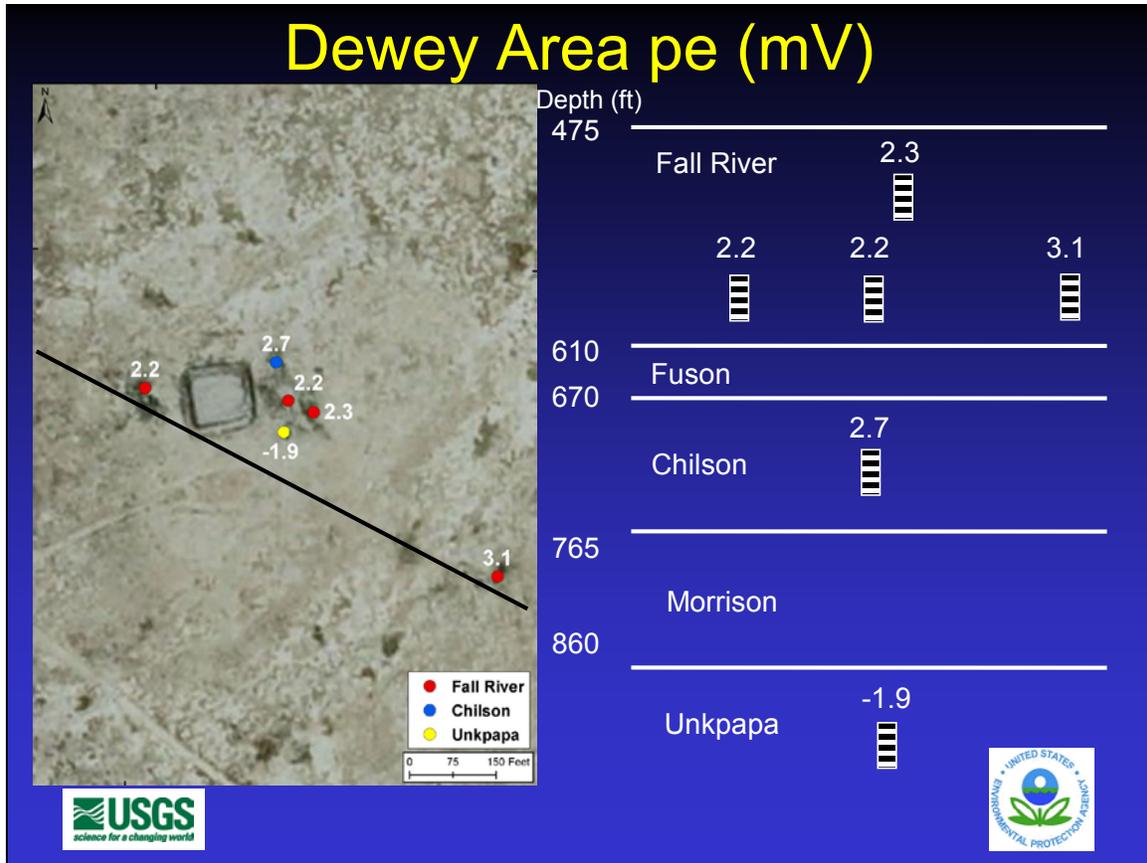
## pe and Dissolved Oxygen (DO)

- pe is a measure of the reducing versus oxidizing conditions
- pe is difficult to measure accurately in the field
  - Need a good redox pair
  - Groundwater is not always in redox equilibrium
- DO is also very difficult to measure in the field, especially at lower concentrations
  - Best to use as a yes/no
- These measurements were done in a flow through cell for best results
- Error is as much at +/- 25-50% or more
- General feel from the data: pe < -0.5 more strongly reducing, pe -0.5 to ~3.0 does not have DO, pe > 3.0 may have DO

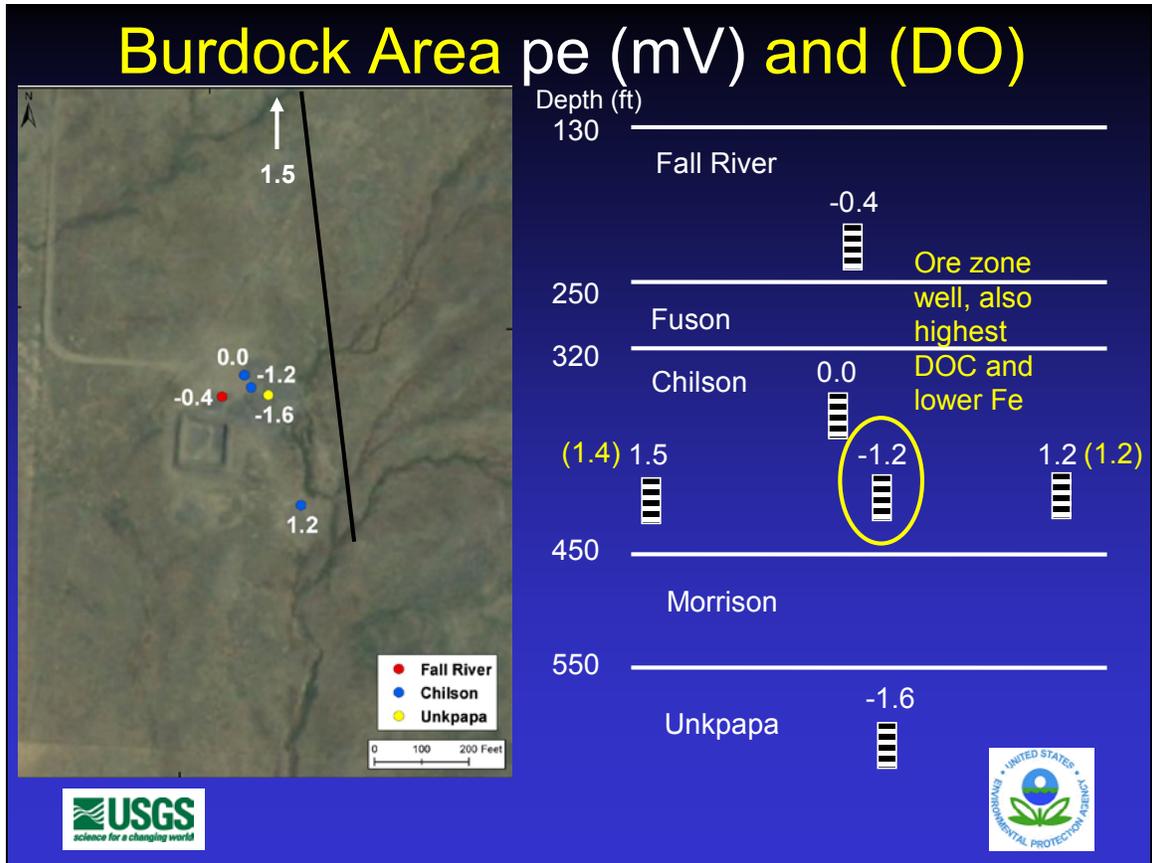




Note that in this slide and subsequent pe/DO slides, ONLY DO that is greater than 1 mg/L is plotted.  
DO < 1 mg/L is not quantitatively detectable with the handheld meter than was used.



No DO was detected.



DOC = dissolved organic carbon.

684 and 682 (wells with DO indicated in parentheses) have some screening in oxidized zone, 680 (circled well) is all in reducing solid phase material.

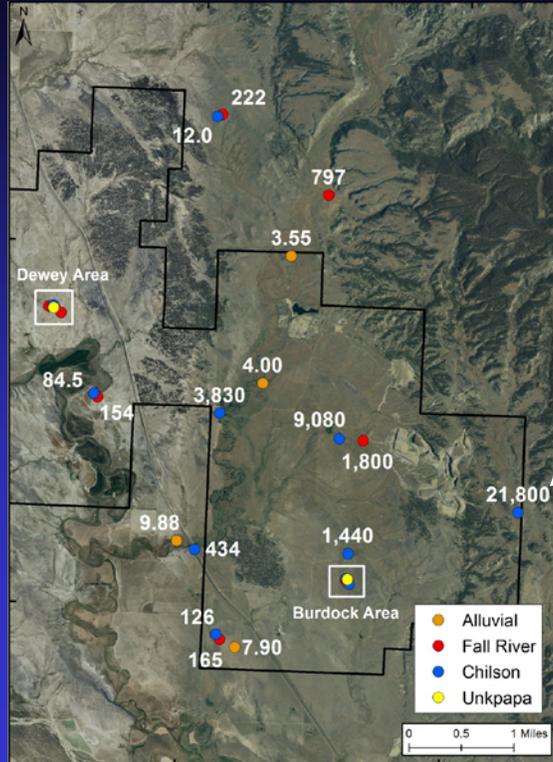
ONLY DO that is greater than 1 mg/L is plotted.

## Iron

- High iron can occur with sulfide oxidation
- Groundwater with dissolved oxygen would not be expected to have much iron
- Groundwater without any dissolved oxygen does not mean that high iron is necessarily expected



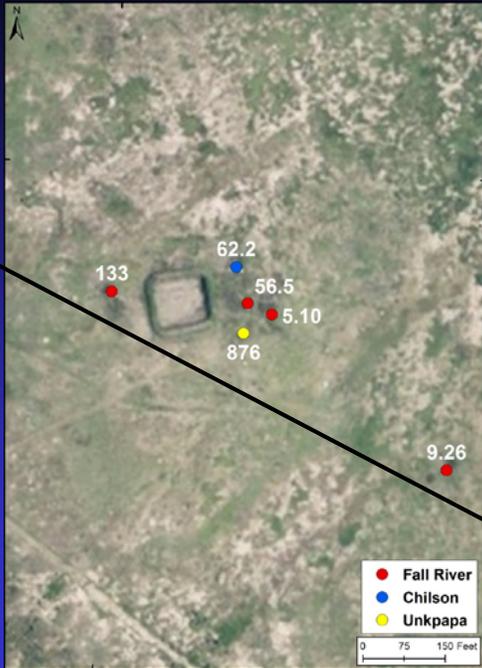
# Iron ( $\mu\text{g/L}$ )



Zone of active sulfide oxidation

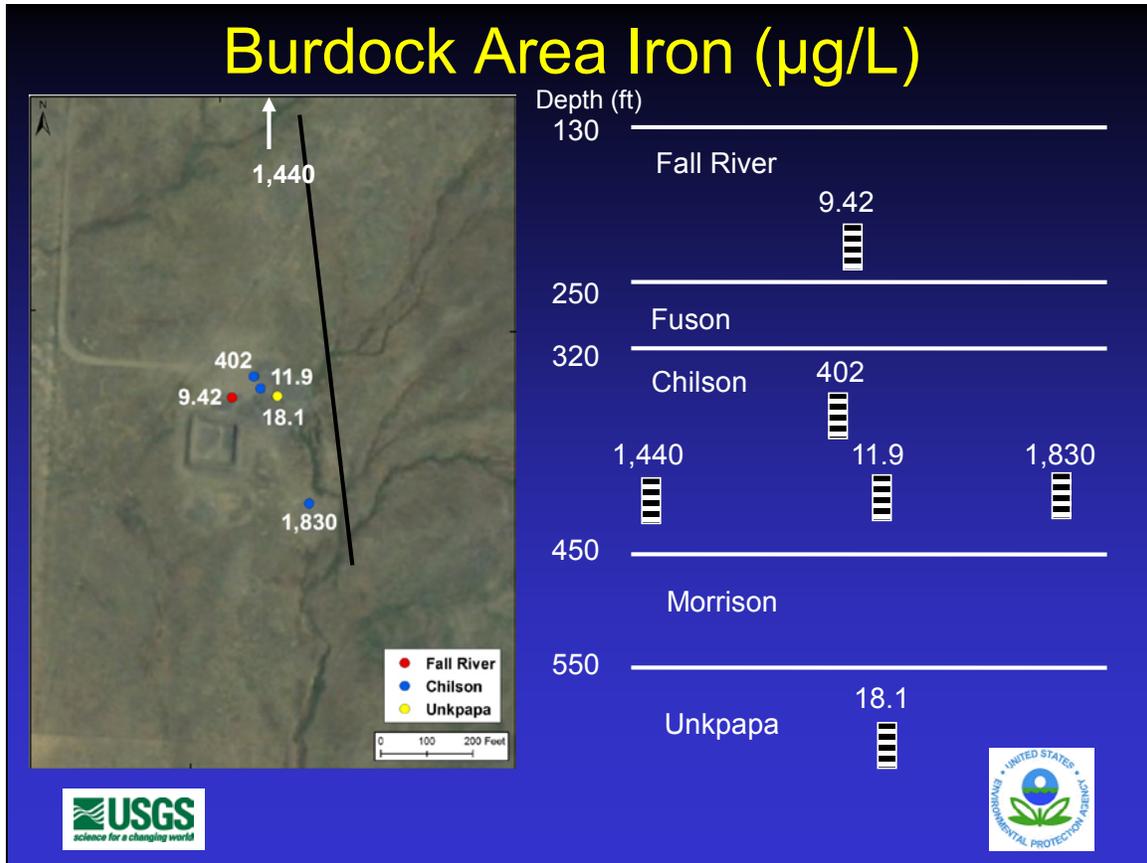


# Dewey Area Iron ( $\mu\text{g/L}$ )



Depth (ft)	Well Name	Iron ( $\mu\text{g/L}$ )
475	Fall River	5.10
	133	133
	56.5	56.5
610	Fuson	
	670	
765	Chilson	62.2
	Morrison	
860	Unkpapa	876





Wells 682 and 684 (14.5 and 22.1 ppb uranium and 1,440 and 1,830  $\mu\text{g/L}$  iron) have some screening in the oxidized zone.

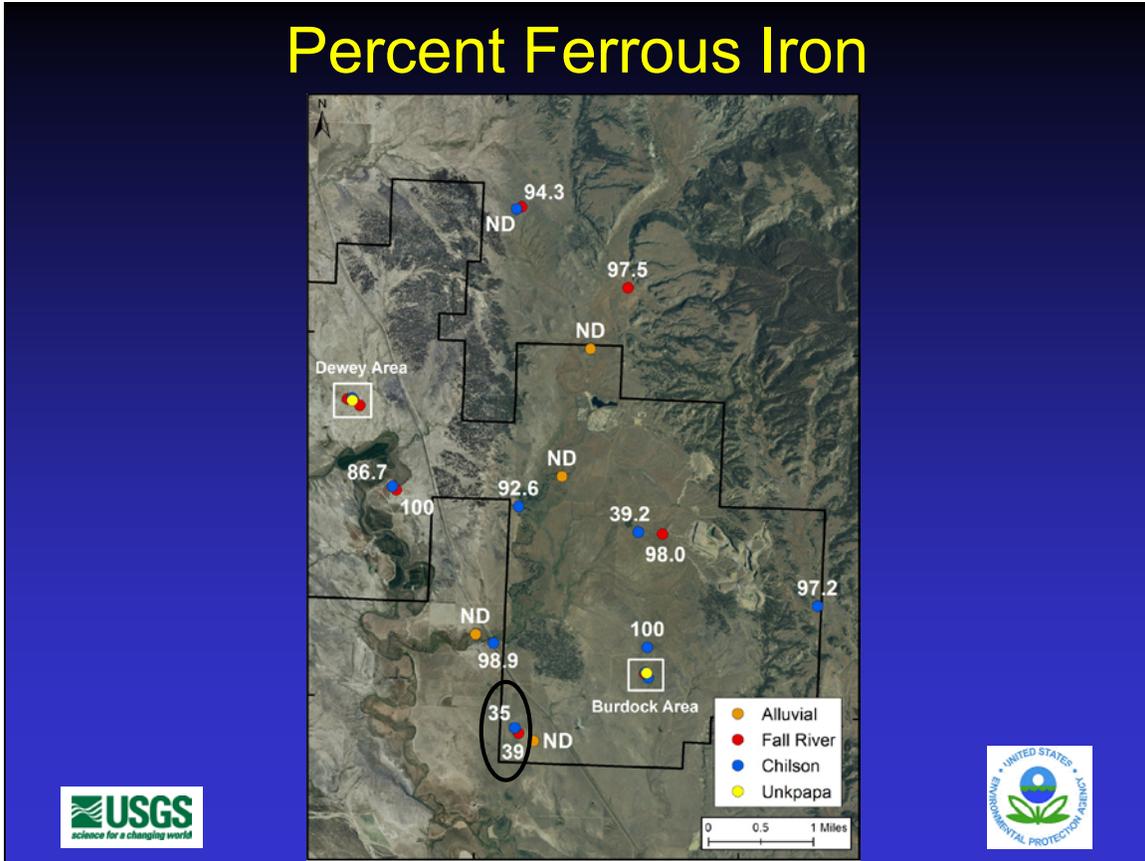
Well 680 (11.9  $\mu\text{g/L}$  iron) is fully screened in a reducing zone.

## Ferrous Iron

- Groundwater without dissolved oxygen would be expected to have a higher amount of ferrous iron vs. ferric iron
- Ferrous iron indicates reducing conditions, ferric iron indicates oxidizing conditions
- Groundwater with low overall iron concentrations may have inaccurate ferrous iron amounts
- Alluvial wells have oxygen and no iron
- Deeper wells do not have oxygen and any iron is mostly ferrous iron



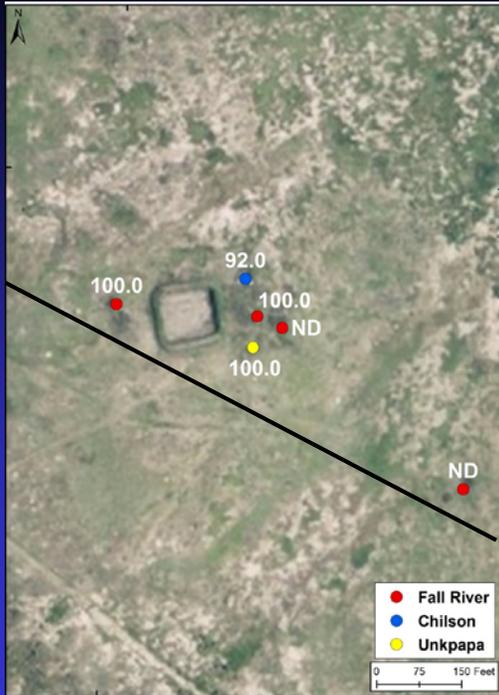
# Percent Ferrous Iron



Circled wells may have inaccurate ferrous iron percentages due to very low overall iron concentrations.

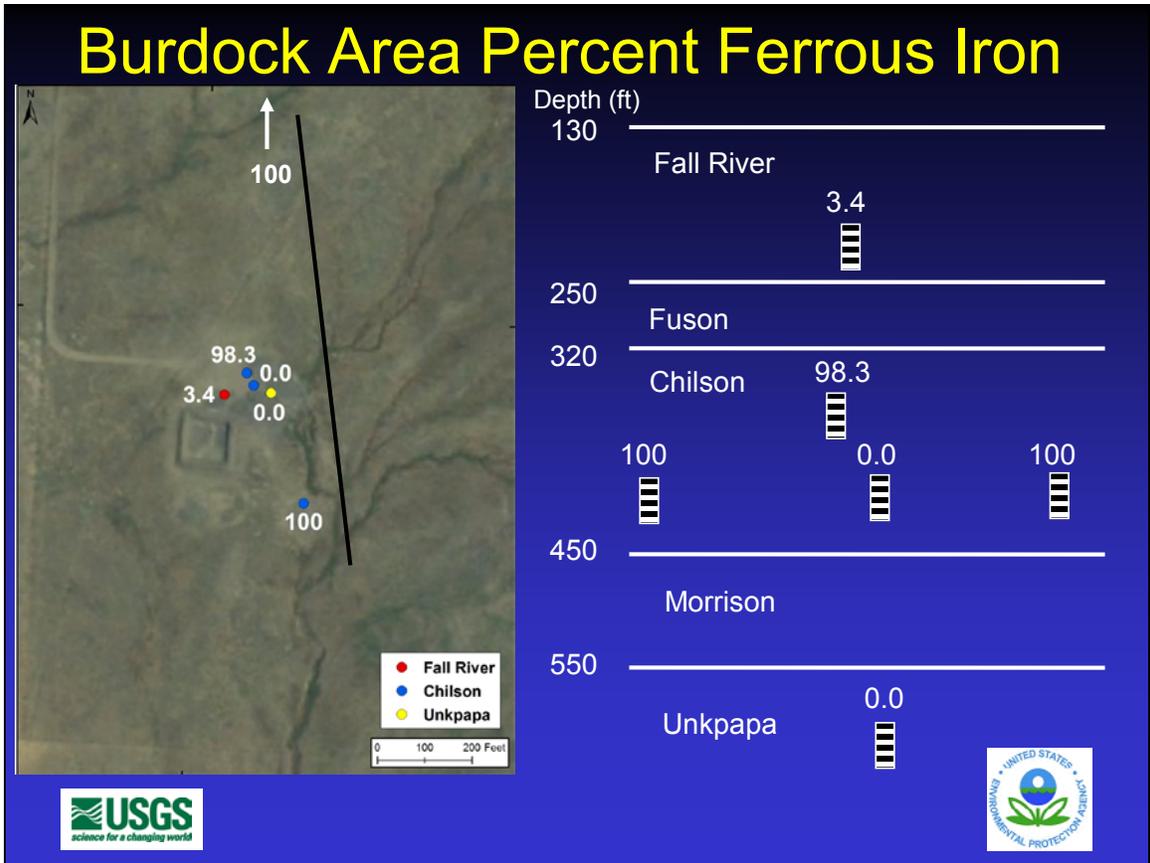
ND = not detected, iron concentrations were below the detection limit.

# Dewey Area Percent Ferrous Iron



Depth (ft)	Location	Value
475	Fall River	100.0
	Chilson	92.0
	Unkpapa	100.0
610	Fuson	100.0
	Chilson	92.0
765	Morrison	ND
	Unkpapa	100.0
860	Unkpapa	100.0

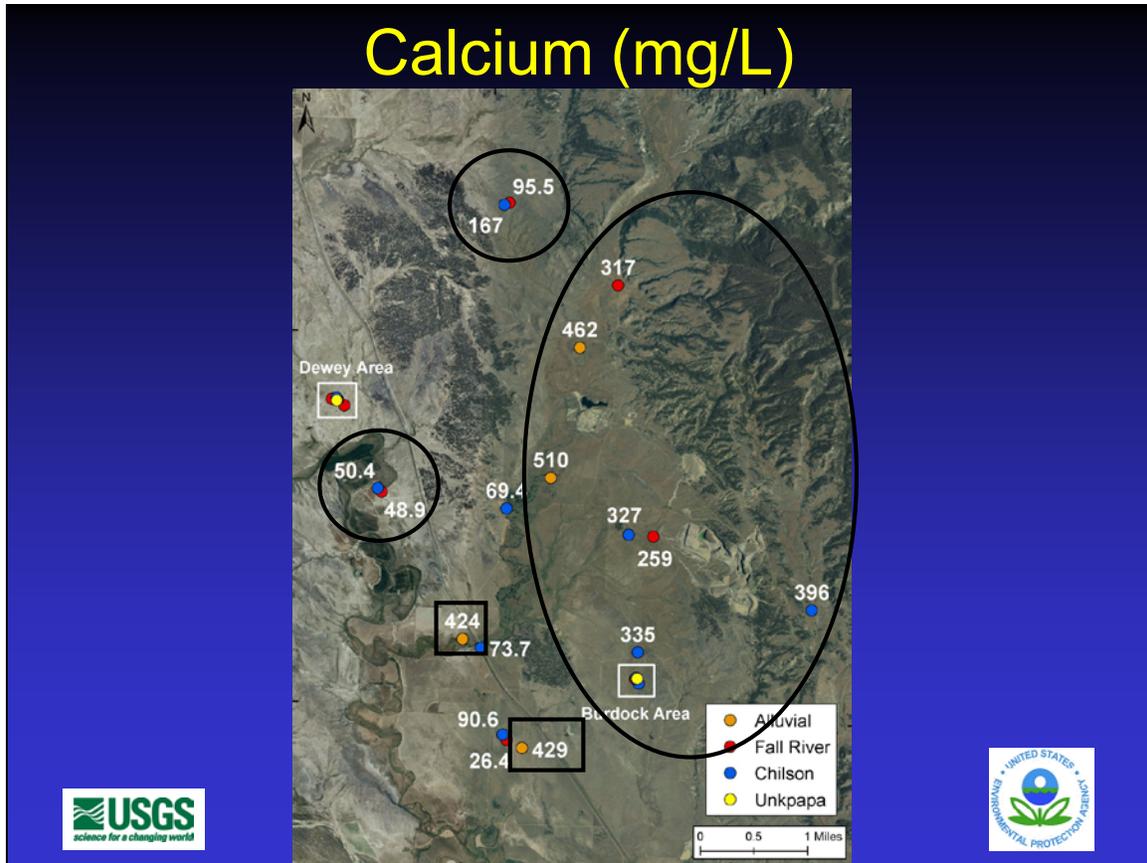




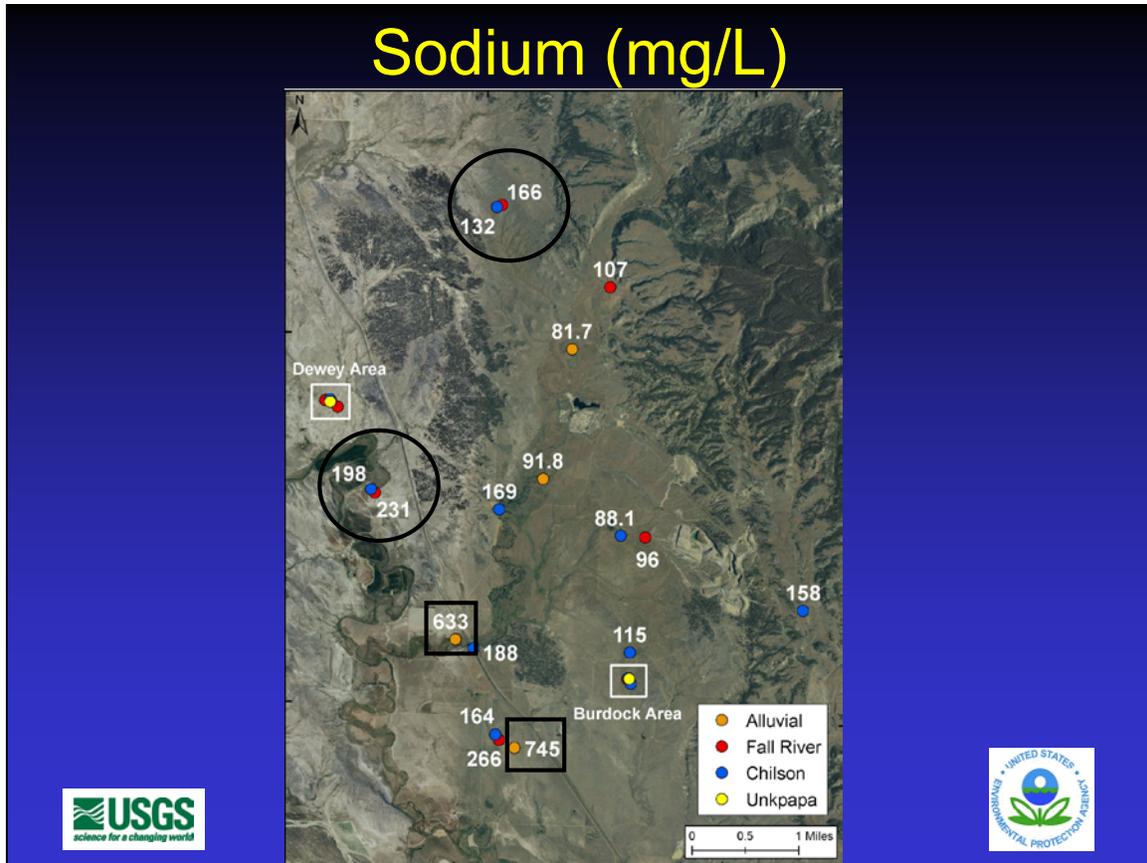
## Calcium and Sodium

- Calcium is controlled by calcite dissolution
- Sodium is most likely from salt dissolution
- Ca and Na ratio may be controlled by cation exchange
- Ca may exchange for Na due to Na-rich clays
- Along a flow path, Ca would decrease and Na would increase





Large circle indicates high calcium values in the Burdock area.  
Rectangles indicate high calcium in alluvial wells.  
Circles indicate lower calcium values in the Dewey area.



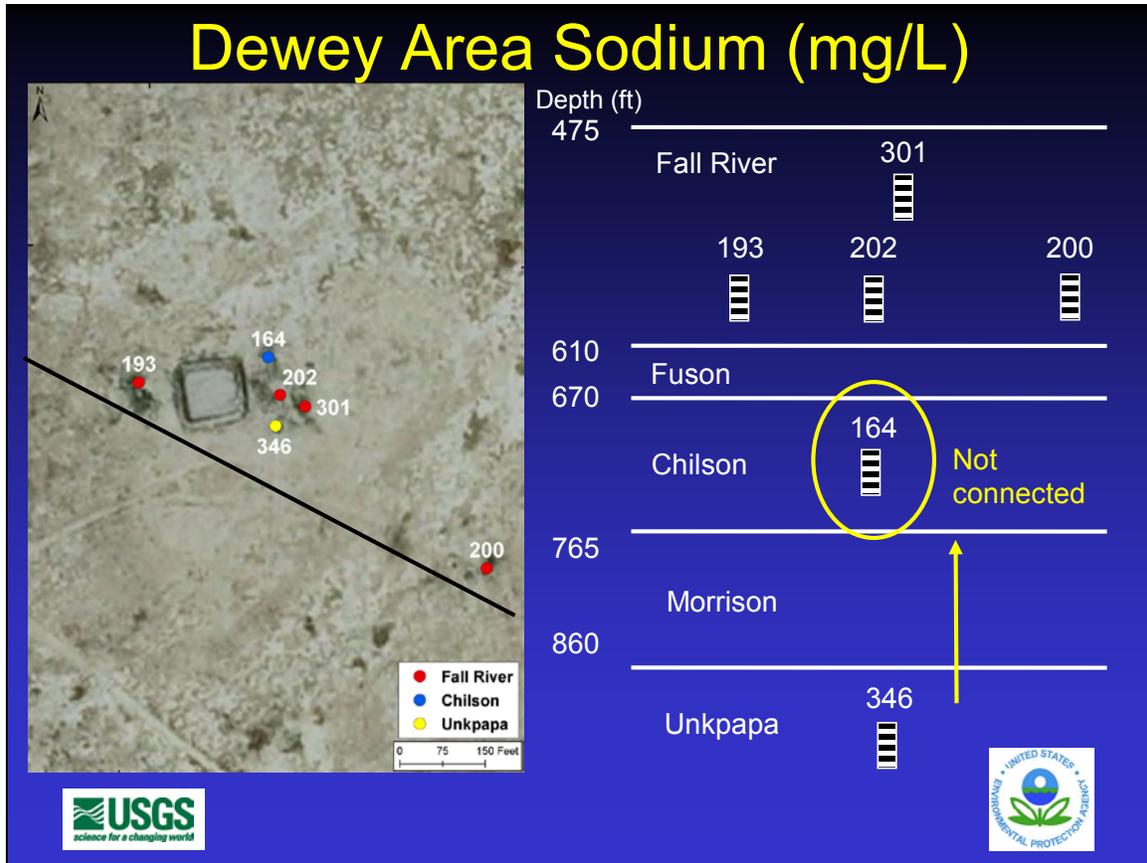
Rectangles indicate high sodium in two alluvial wells.  
Circles indicate slightly higher sodium in the Dewey area.

# Dewey Area Calcium (mg/L)



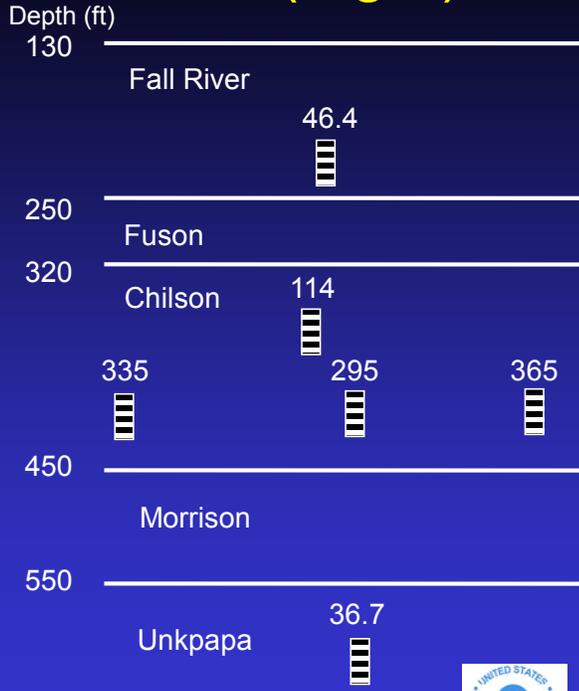
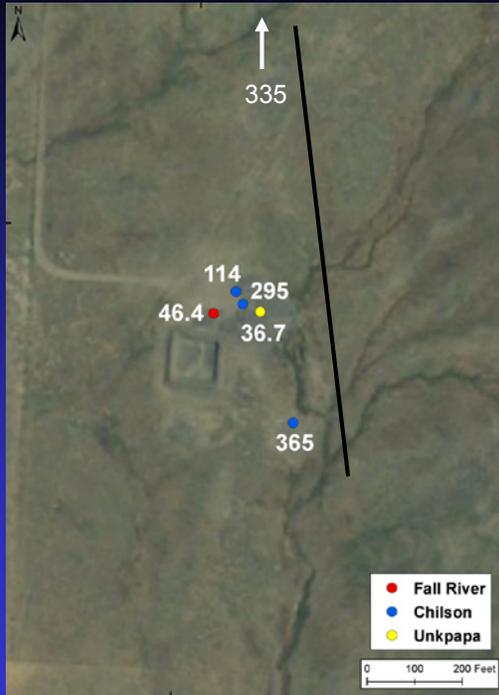
Depth (ft)	Well Name	Calcium (mg/L)
475	Fall River	4.96
	Fall River	68.4
	Fall River	58.9
610	Fuson	56.9
	Fuson	65.2
670	Chilson	42.7
	Chilson	58.9
765	Morrison	56.9
	Morrison	65.2
860	Unkpapa	65.2
	Unkpapa	42.7

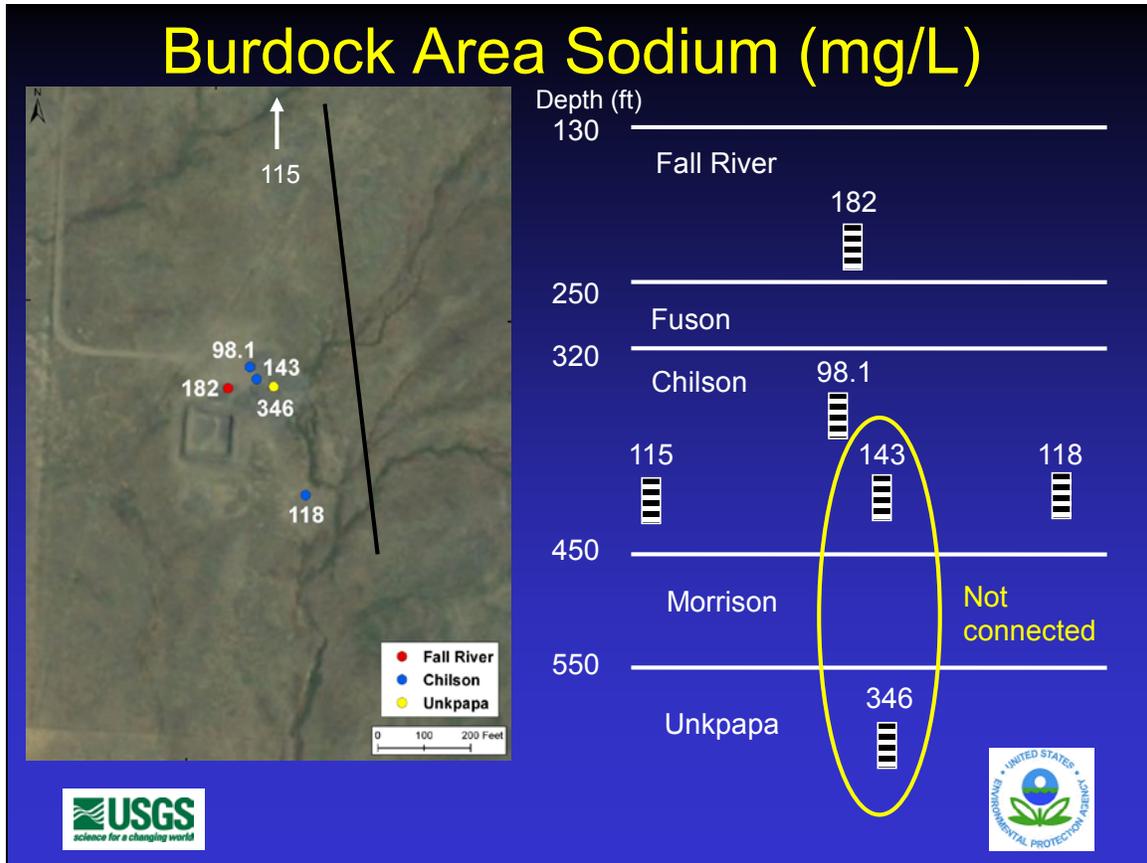




Sodium should be relatively conservative (or if anything should increase), so significant upward flow of groundwater from the Unkpapa is not indicated.

# Burdock Area Calcium (mg/L)





Sodium should be relatively conservative (or if anything should increase), so significant upward flow of groundwater from the Unkpapa is not indicated.

## Groundwater Geochemistry Summary and Interpretations

- From the geochemistry, no evidence of natural groundwater flow across units in the project area (variety of indicators)
- No evidence of breccia pipes in project area
- Alluvial groundwater is not connected to the rest of the system (variety of indicators)
- Recharge under Pass Creek could be a significant source of water, oxygen, and tritium
- Groundwaters away from Pass Creek and alluvium are mostly greater than 60 years old (no tritium)



For the first point, this does not mean that pumping could not create a connection! Breccia pipes would provide a potential pathway for groundwater flow across confining units.

## Groundwater Geochemistry Summary and Interpretations (cont.)

- Source of groundwater recharge away from Pass Creek is unclear (dramatic  $^{18}\text{O}$  differences)
- Major geochemistry (Ca, Na, and Sulfate) differences between Dewey and Burdock areas may be due to different recharge conditions and not ion exchange, but cation exchange could still occur downgradient
- Groundwater flow downgradient from the Burdock unit may lie more to the south than originally thought (based on placement of well 696)

