APP-026

Slide 1

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

Slide 2

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

By Raymond H. Johnson

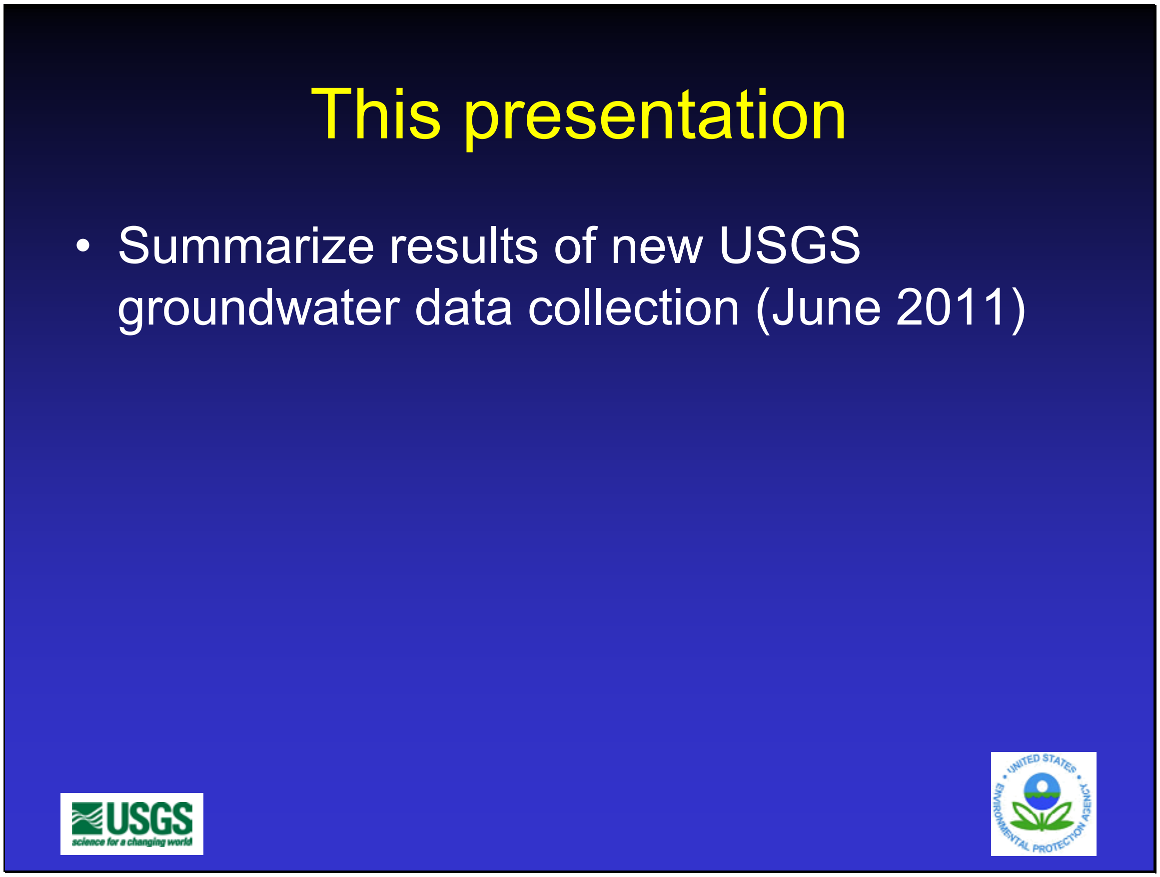
Slide 3

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

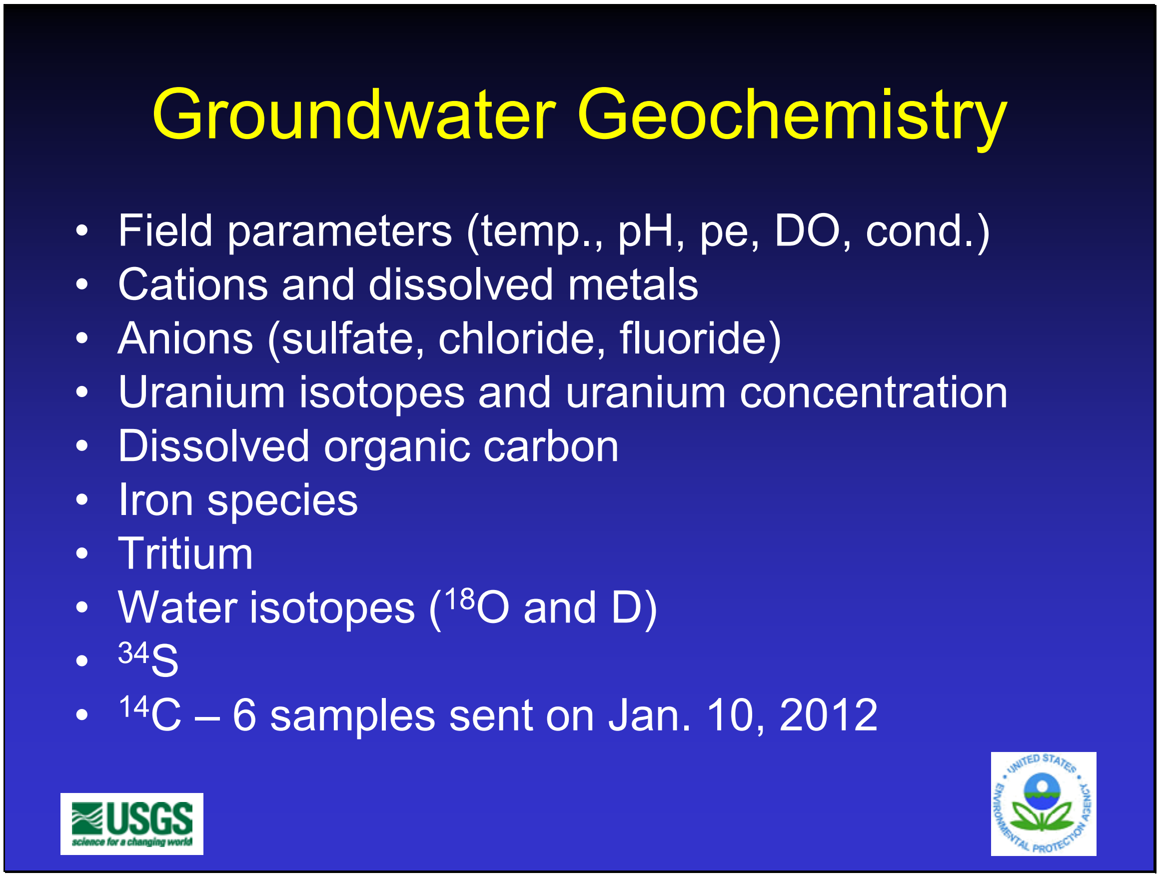
Before doing more detailed reactive transport modeling, this presentation presents information on the current groundwater flow system based on groundwater geochemistry.

Slide 4



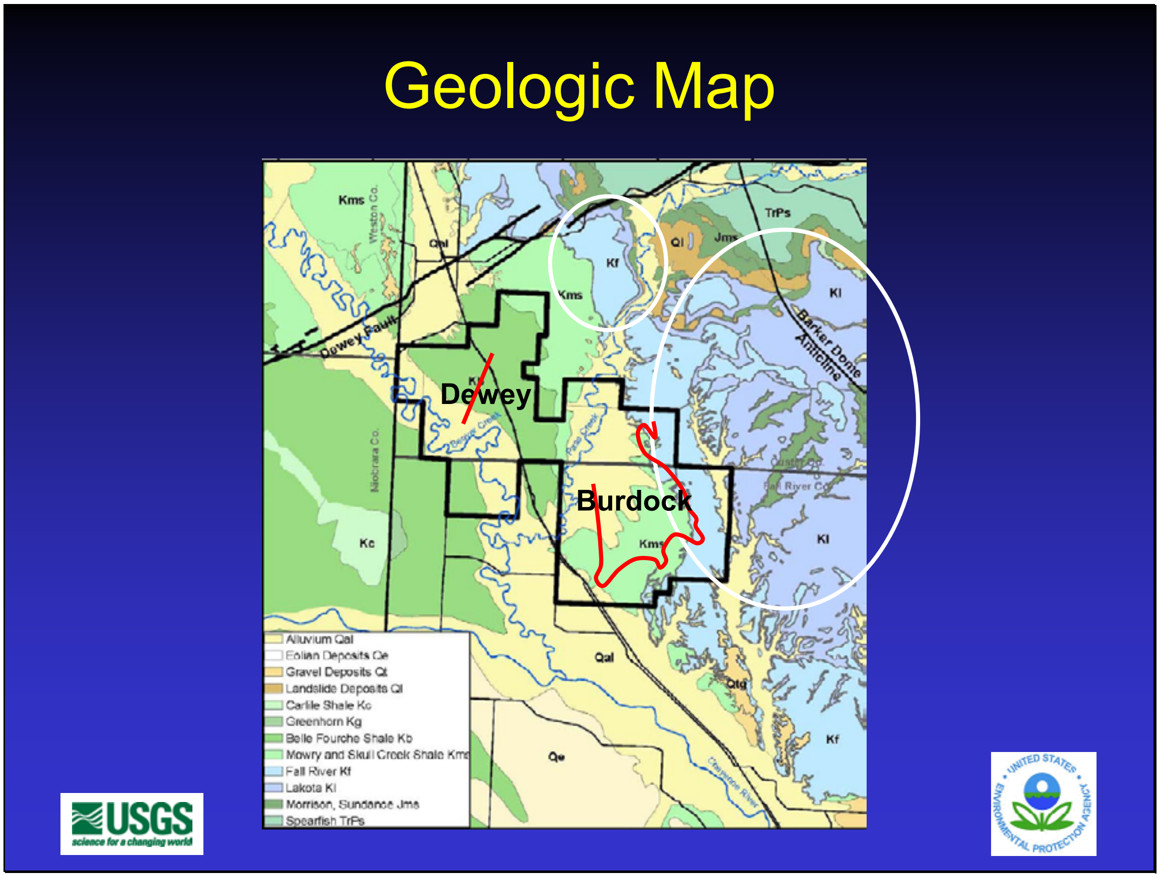
These data were collected to support better understanding of the current groundwater flow system and to use in more detailed reactive transport (presentation #5 in this series).

Slide 5



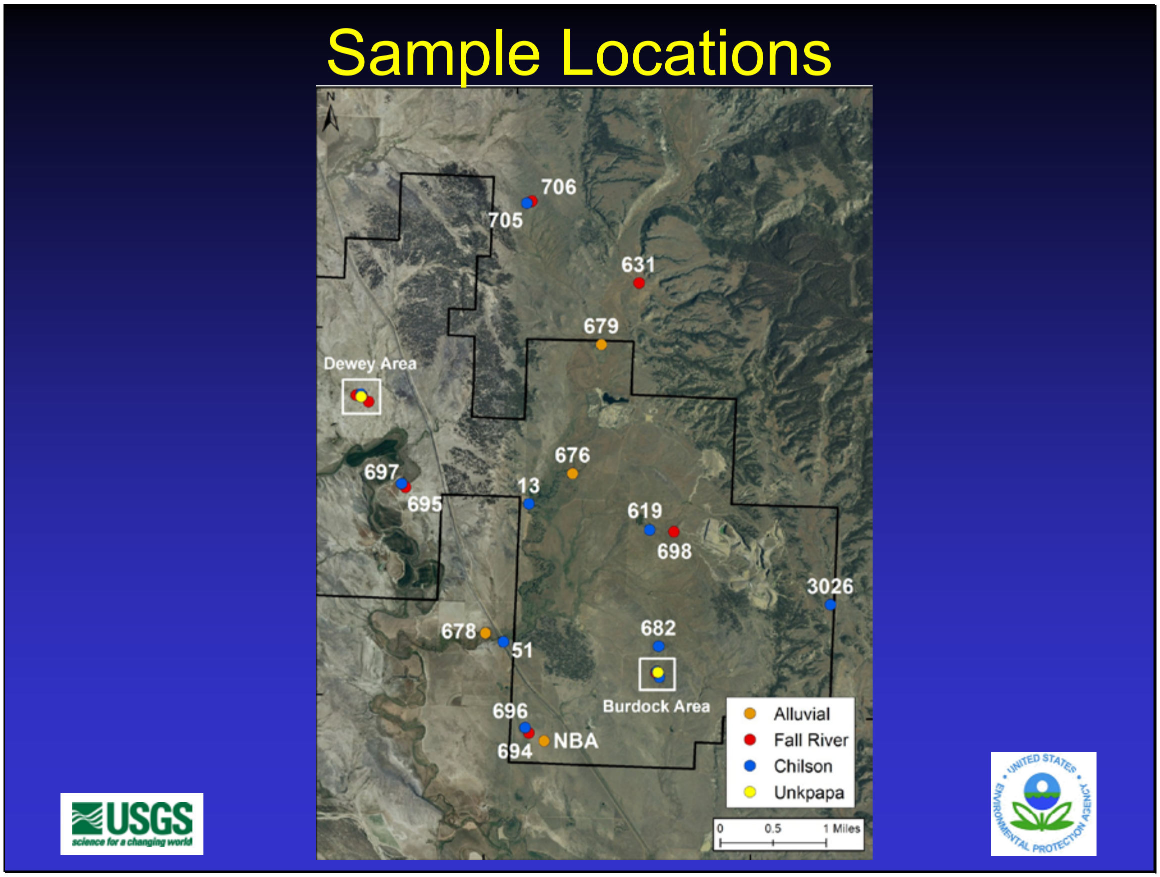
This is the list of the types of groundwater geochemistry data that were collected.
In the following slides, an introduction slide is included for each constituent on how it is used for interpretations.

Slide 6



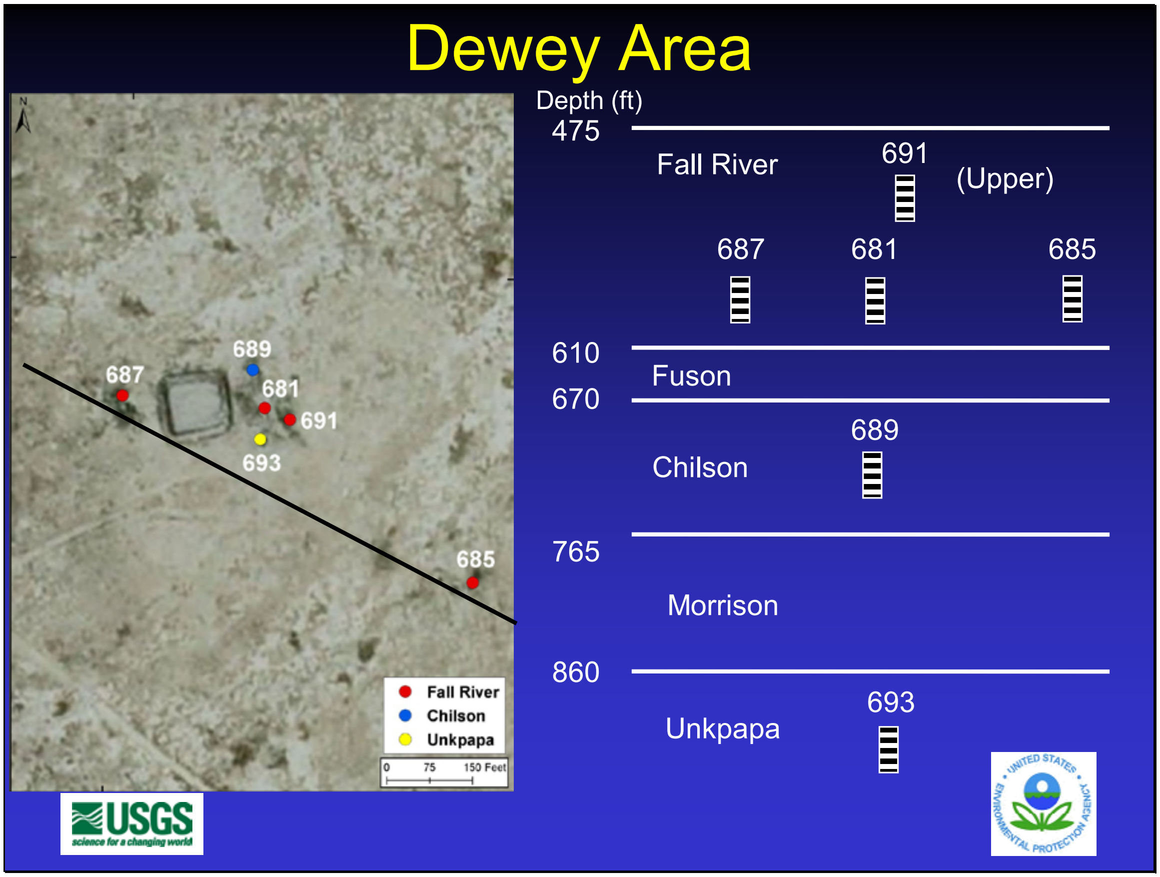
The white circles indicate the recharge zone for the Fall River Formation (left) and the Lakota Formation (right).
The Fall River recharge area is quite small and close to Pass Creek; whereas, the Lakota recharge area is much larger and forms a separate drainage area.
Red lines indicate ore zones. Dewey area is in the Fall River Formation and Burdock area is in the Lower Chilson Member of the Lakota Formation.

Slide 7



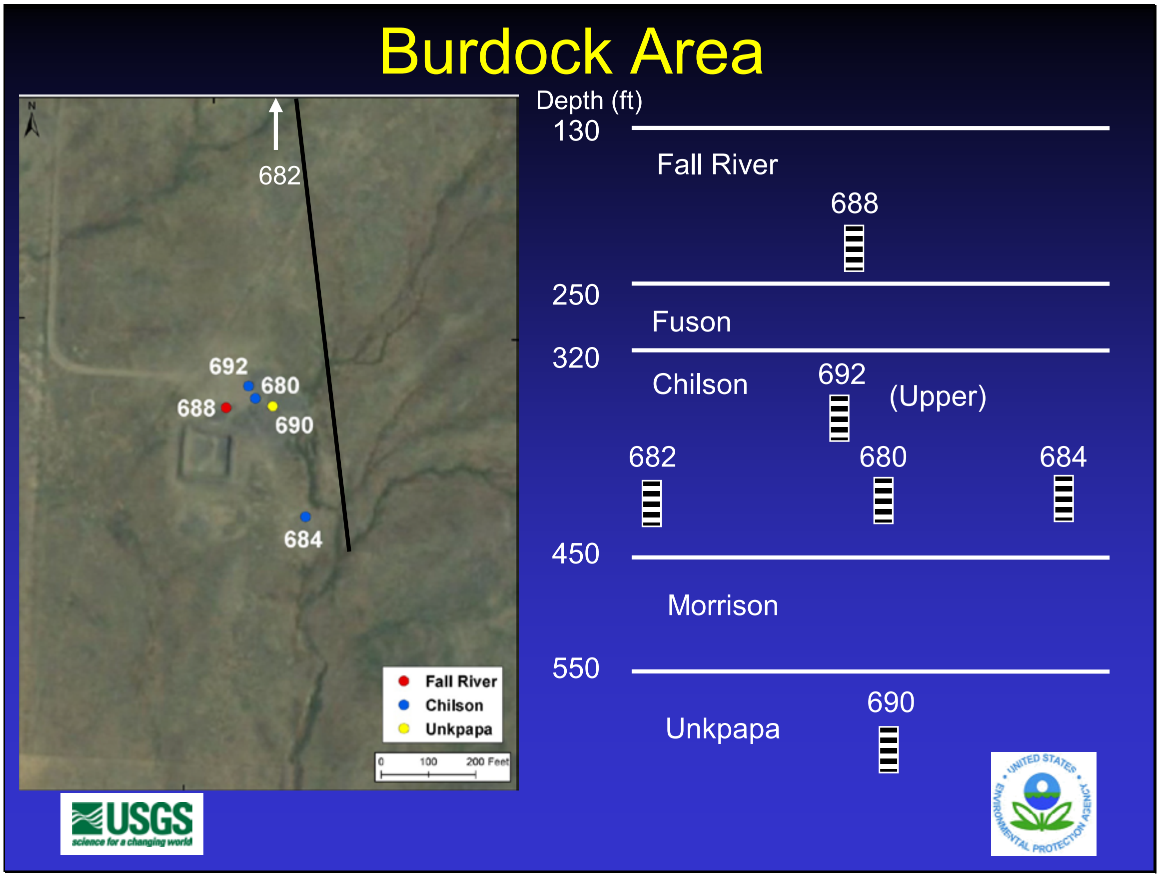
All of these sample locations are from existing wells. Locations were selected to get a good overall area representation.

Slide 8



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.

Slide 9



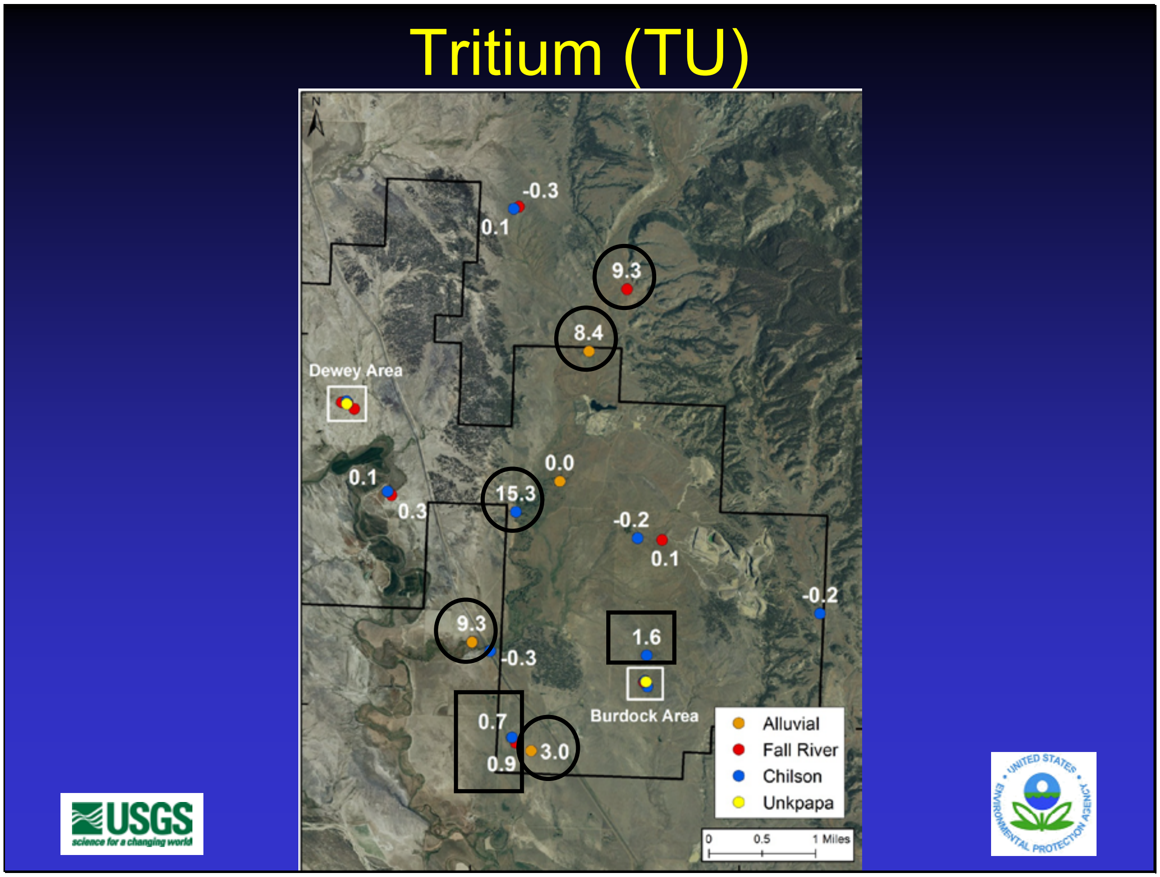
Location of well 682 is shown in slide #7.

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

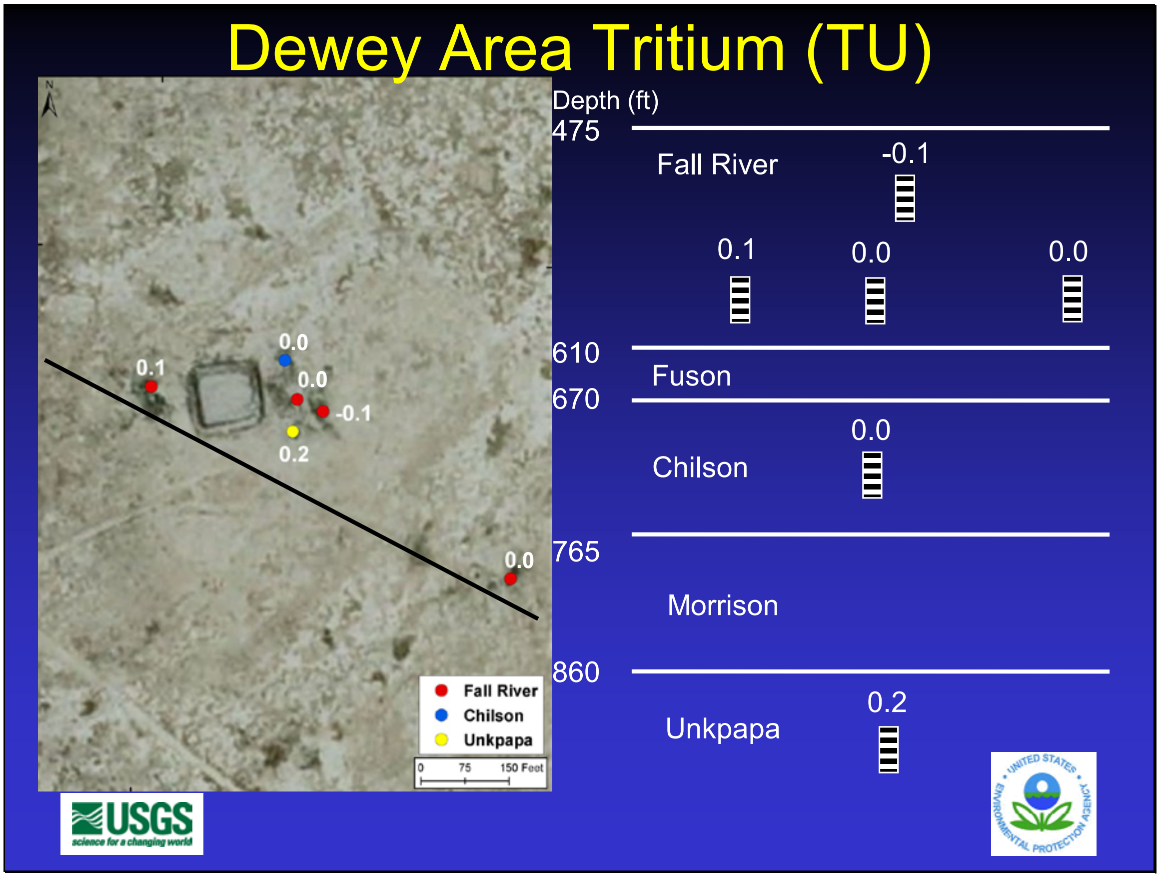
SD = standard deviation.
TU = tritium units.
If no tritium – 60 years old or older.
If some tritium – possibility that it could be older because of contamination during TVA (Tennessee Valley Authority) exploration.

Slide 11



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.

Slide 12


Dewey Area Tritium (TU)
Depth (ft)
475
Fall River
-0.1
0.1
0.0
0.0
610
Fuson
670
Chilson
0.0
765
Morrison
860
Unkpapa
0.2
0.1
0.0
0.0
-0.1
0.2
0.0
Fall River
Chilson
Unkpapa
0 75 150 Feet
USGS
science for a changing world
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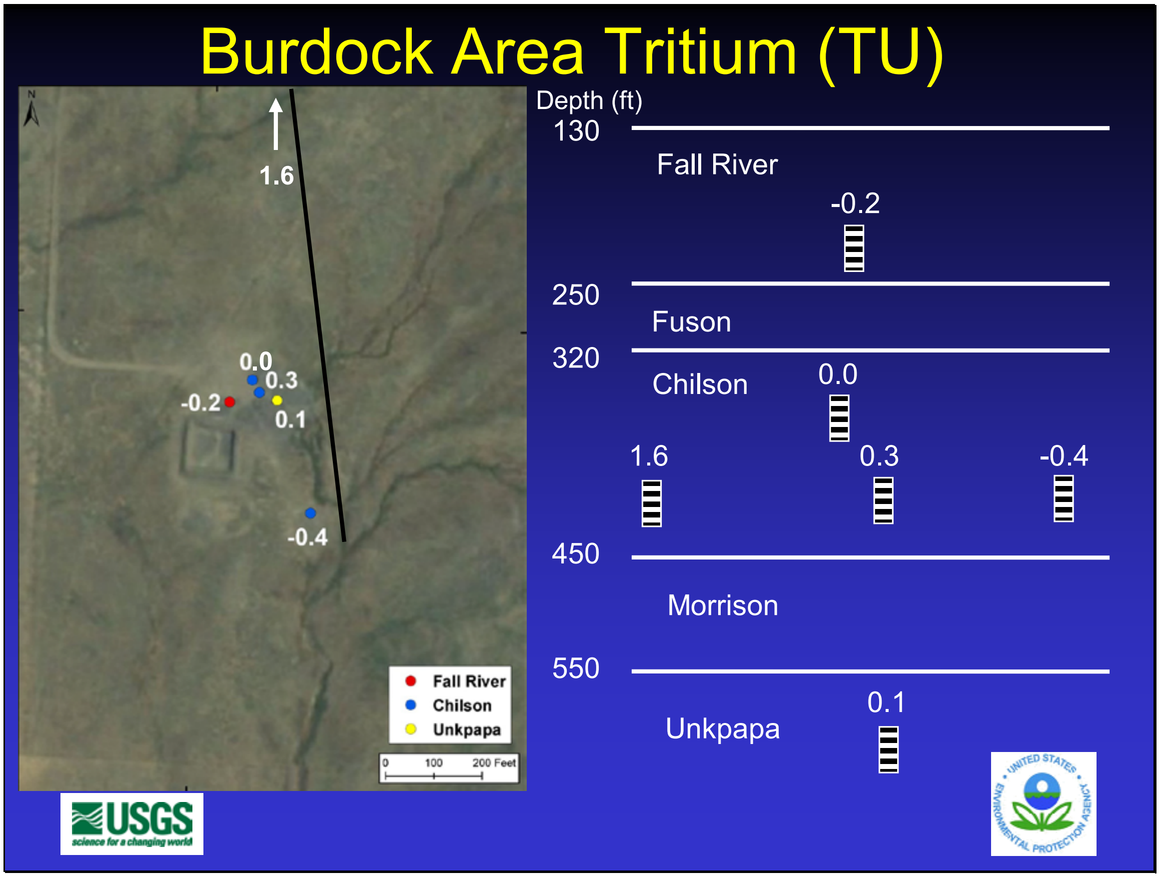
Slide 13


Burdock Area Tritium (TU)
1.6
0.0
0.3
-0.2
0.1
-0.4
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
-0.2
250
Fuson
320
Chilson
0.0
1.6
0.3
-0.4
450
Morrison
550
Unkpapa
0.1
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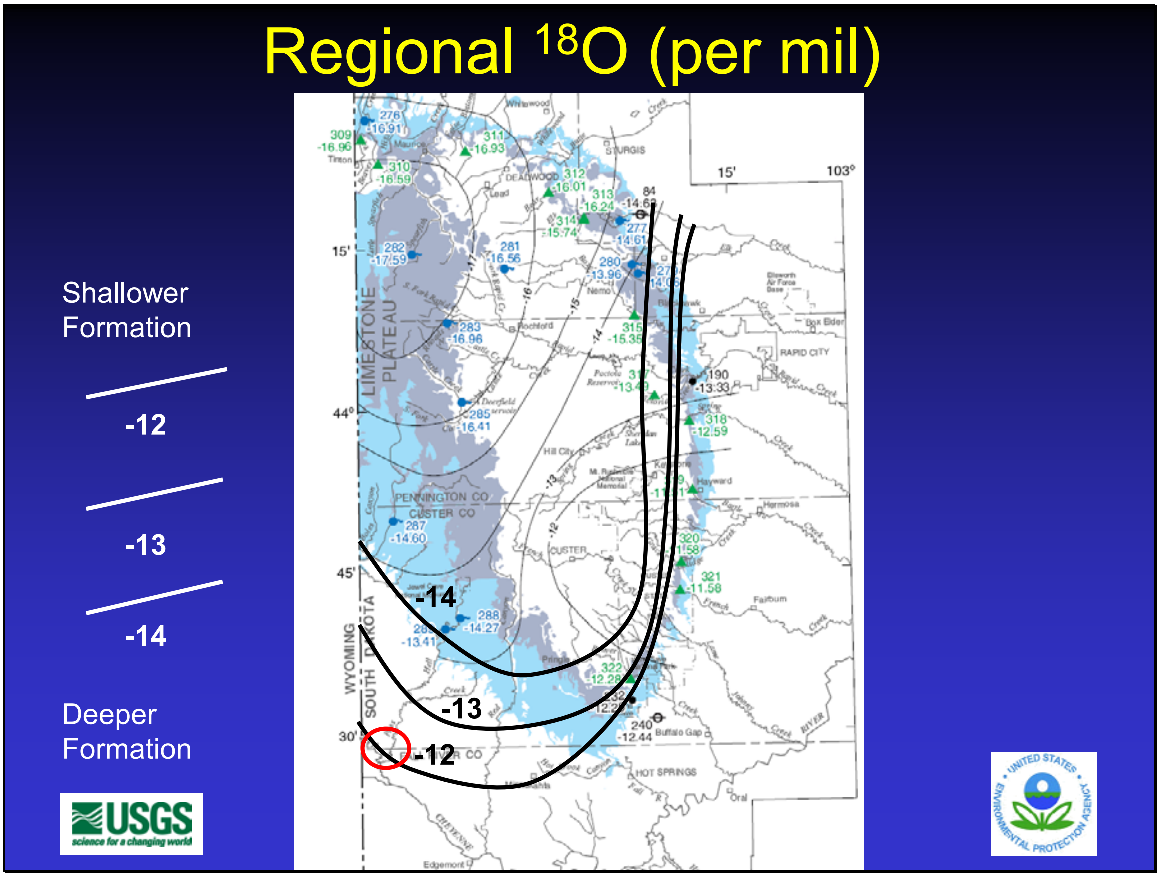
Slide 14

^{18}O

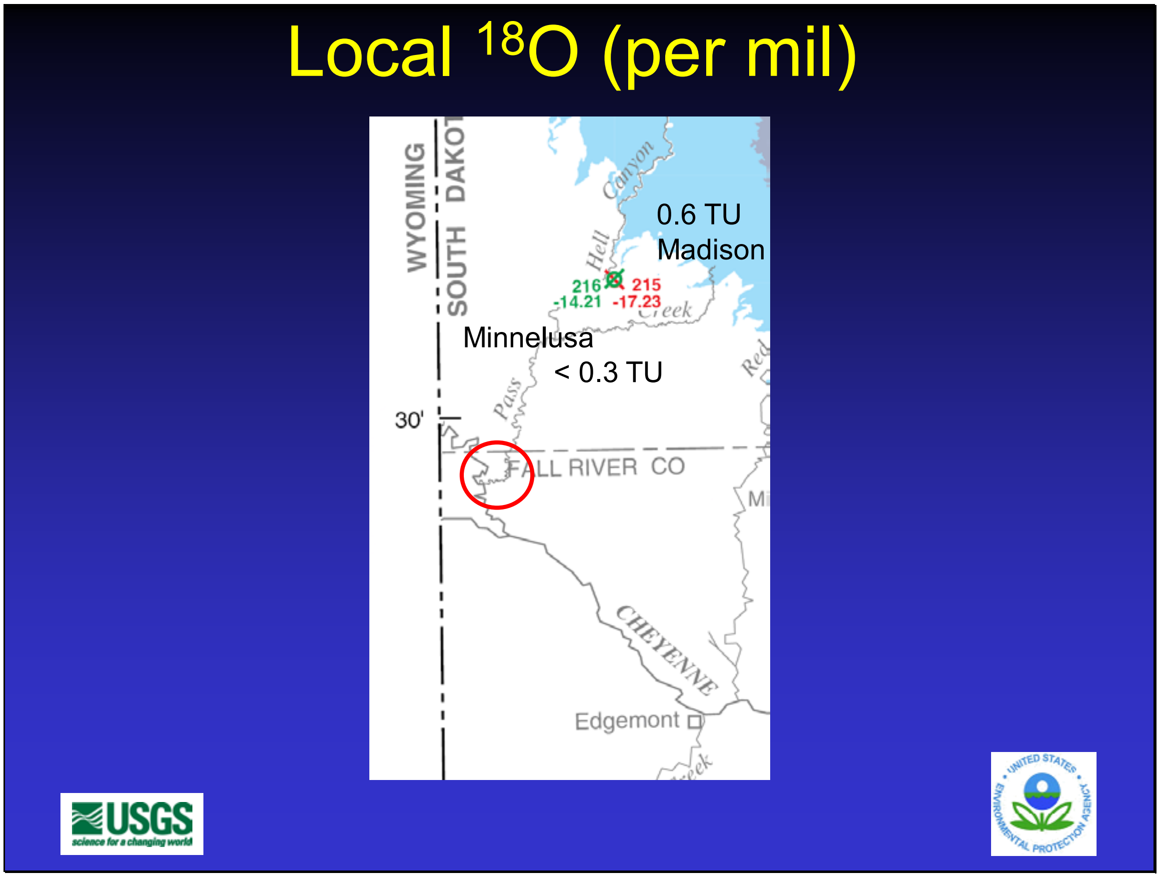
- Naturally occurring stable water isotope
- Conservative tracer, not reactive
- More negative at higher altitude (or during a colder climate)
- Good tracer for recharge source
- Good tracer for evidence of aquifer connections
- Error (1 SD) of about +/- 0.06 per mil
- Do not have direct data for Pass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

SD = standard deviation.
Not reactive indicates that the isotopic value does not changes once recharge water becomes groundwater.



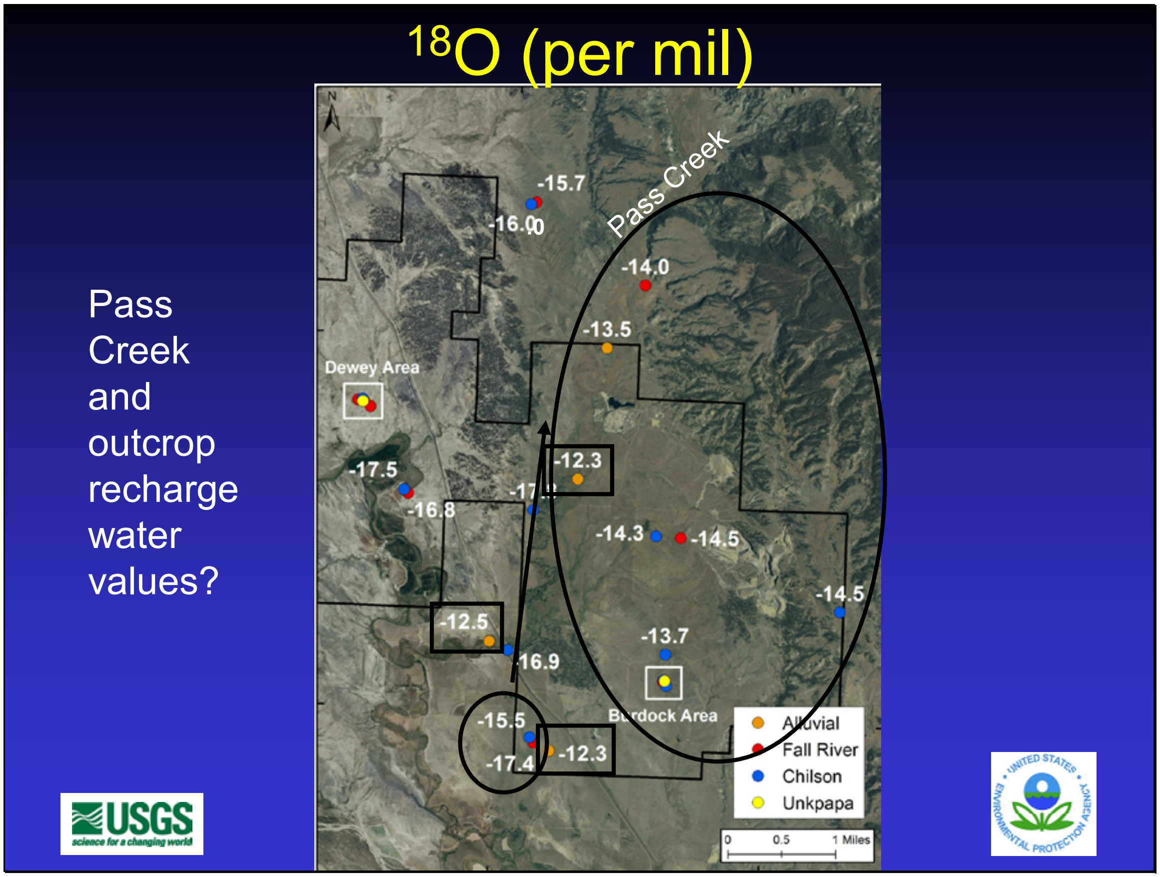
Data is from wells, springs, and stream flow.
Map is from Black Hills Regional Hydrology Study by the USGS, reference is:
Naus, C.A., Driscoll, D.G., and Carter, J.M., 2001, Geochemistry of the Madison and Minnelusa aquifer in the Black Hills area, South Dakota: U.S. Geological Survey, Water-Resources 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.

Slide 16



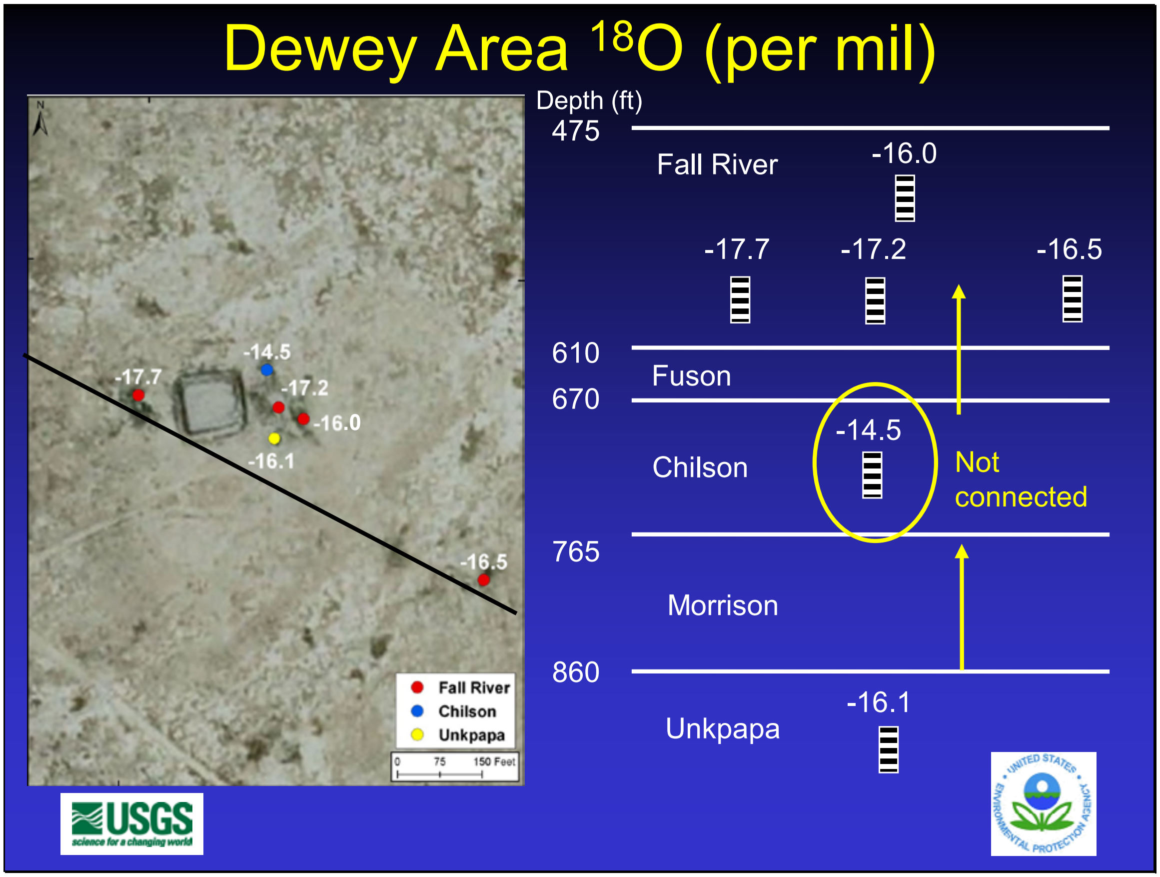
Red circle = site area.
The Madison is a deep karstic limestone (below the Minnelusa) and is presumably recharged at higher elevation (thus lower oxygen isotope value). Karstic nature may allow for fast transport of groundwater, thus the 0.6 TU value for tritium.
Map is modified from the Black Hills 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.

Slide 17



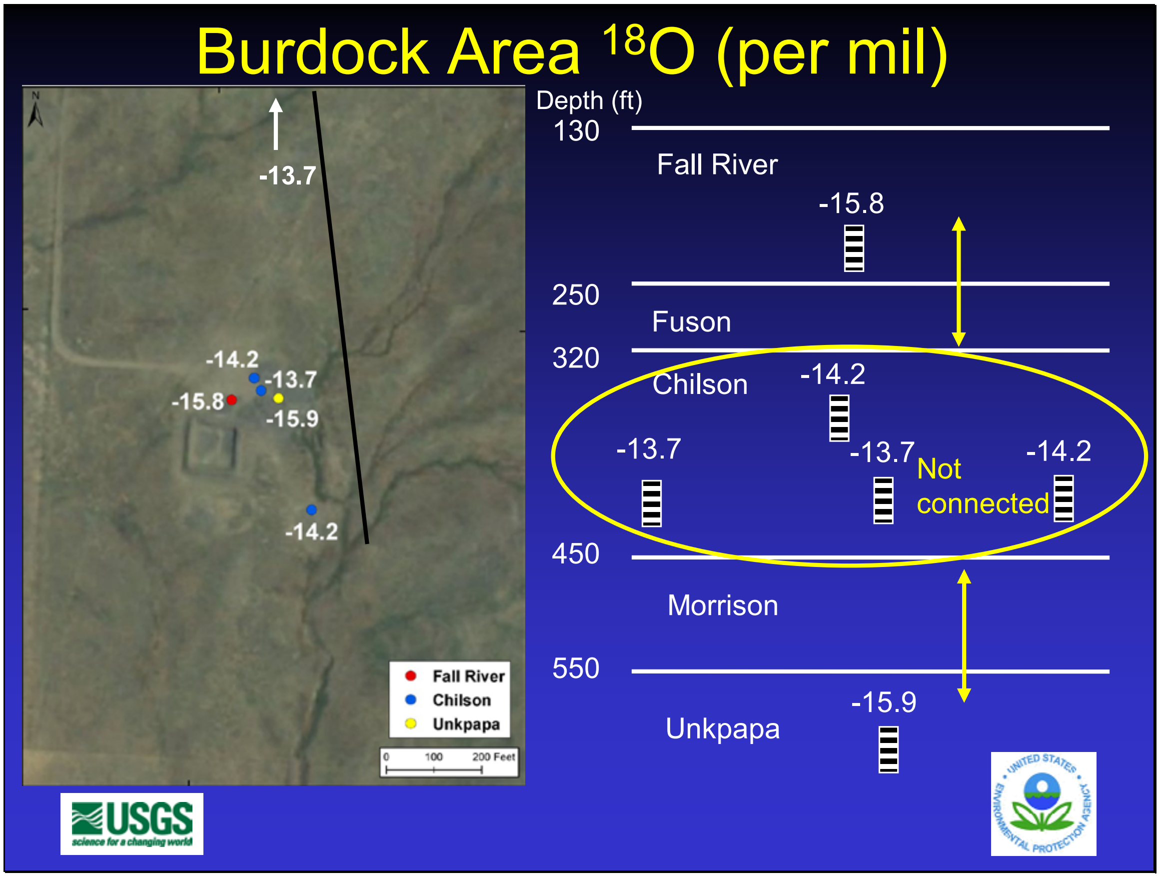
Samples for local precipitation and local streams are not available.
Rectangles indicate alluvial wells that are likely recharged locally (^{18}O near -12), which makes sense based on slide #15. Any values that are more negative are probably groundwater that is not derived from local recharge (although 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.

Slide 18



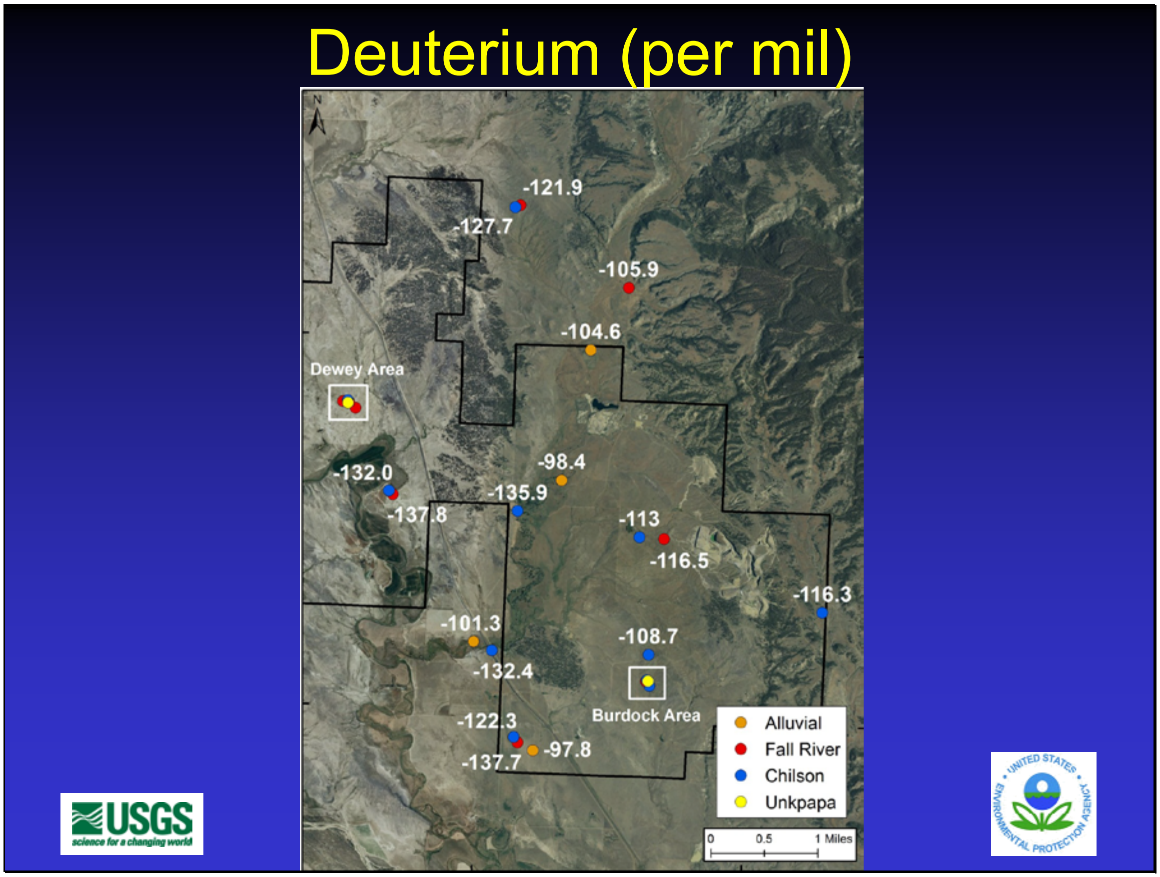
This area has upward hydraulic heads (40 ft. higher in the Chilson than the Fall River); however, oxygen isotopes do not indicate a strong transfer of water across the local aquitards (Fuson and Morrison), albeit only one sample is available in the Chilson.

Slide 19



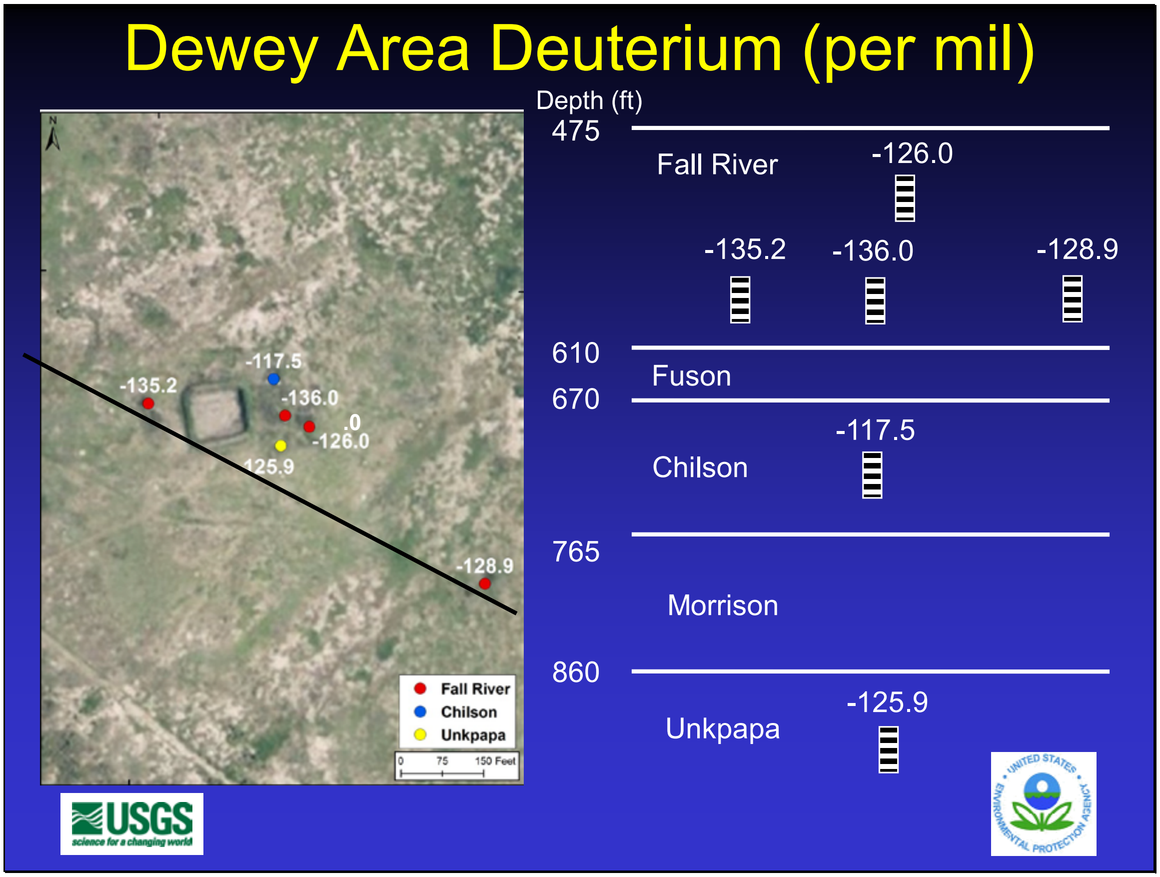
Double arrows indicate that there is no significant hydraulic head across the units. Oxygen isotopes do not indicate a strong transfer of water across the local aquitards (Fuson and Morrison).

Slide 20



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

Slide 21


Dewey Area Deuterium (per mil)
-117.5
-135.2
-136.0
.0
-126.0
125.9
-128.9
Fall River
Chilson
Unkpapa
0 75 150 Feet
Depth (ft)
475
Fall River
-126.0
-135.2
-136.0
-128.9
610
Fuson
670
-117.5
Chilson
765
Morrison
860
-125.9
Unkpapa
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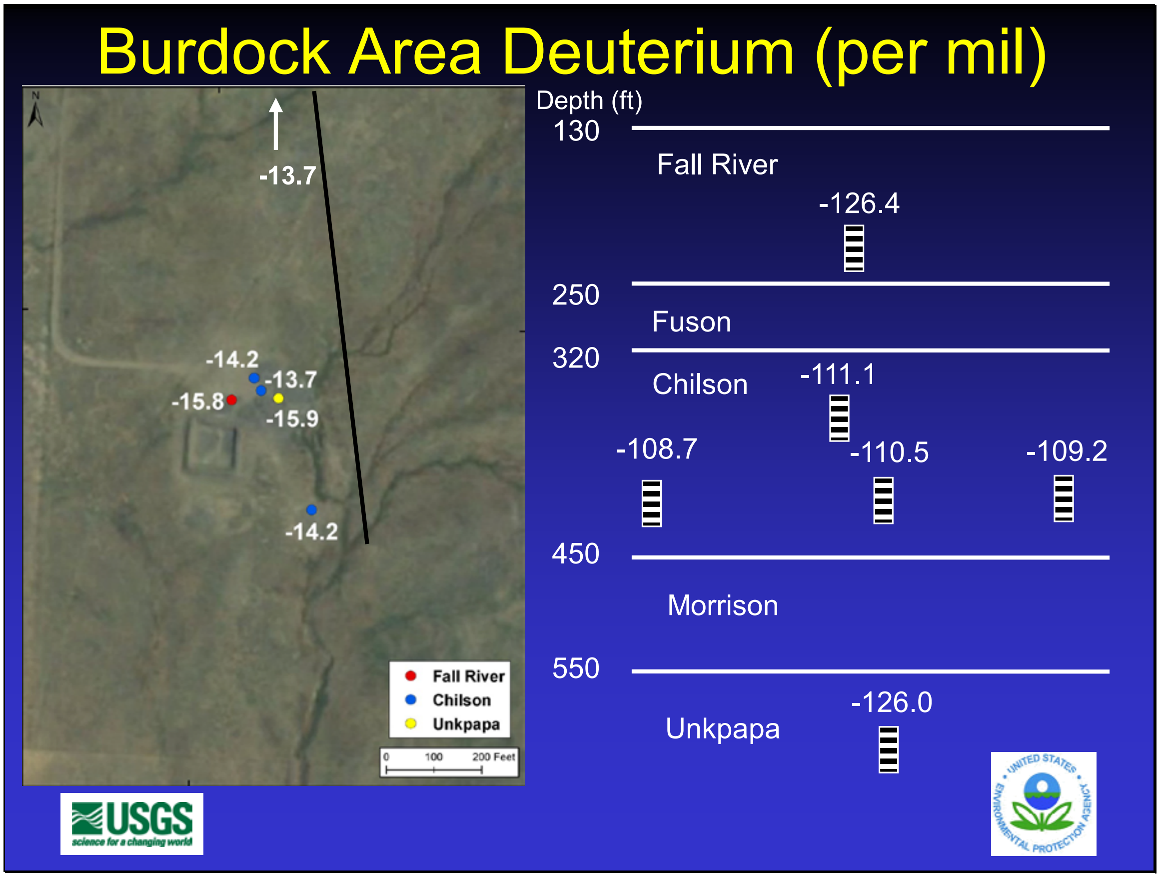
Slide 22



Burdock Area Deuterium (per mil)
-13.7
-14.2
-13.7
-15.8
-15.9
-14.2
Fall River
Chilson
Unkpapa
0 100 200 Feet
Depth (ft)
130
Fall River
-126.4
250
Fuson
320
Chilson
-111.1
-108.7
-110.5
-109.2
450
Morrison
550
Unkpapa
-126.0
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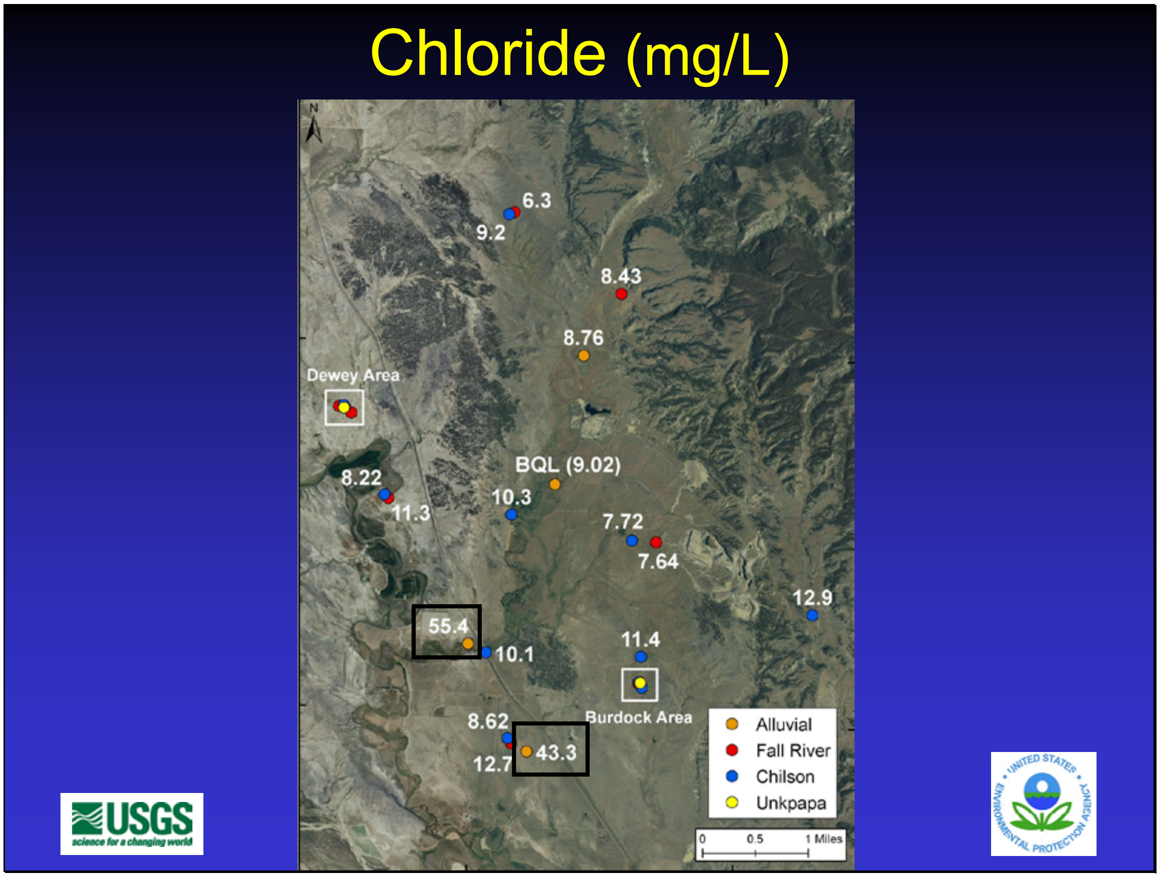
Slide 23

Chloride

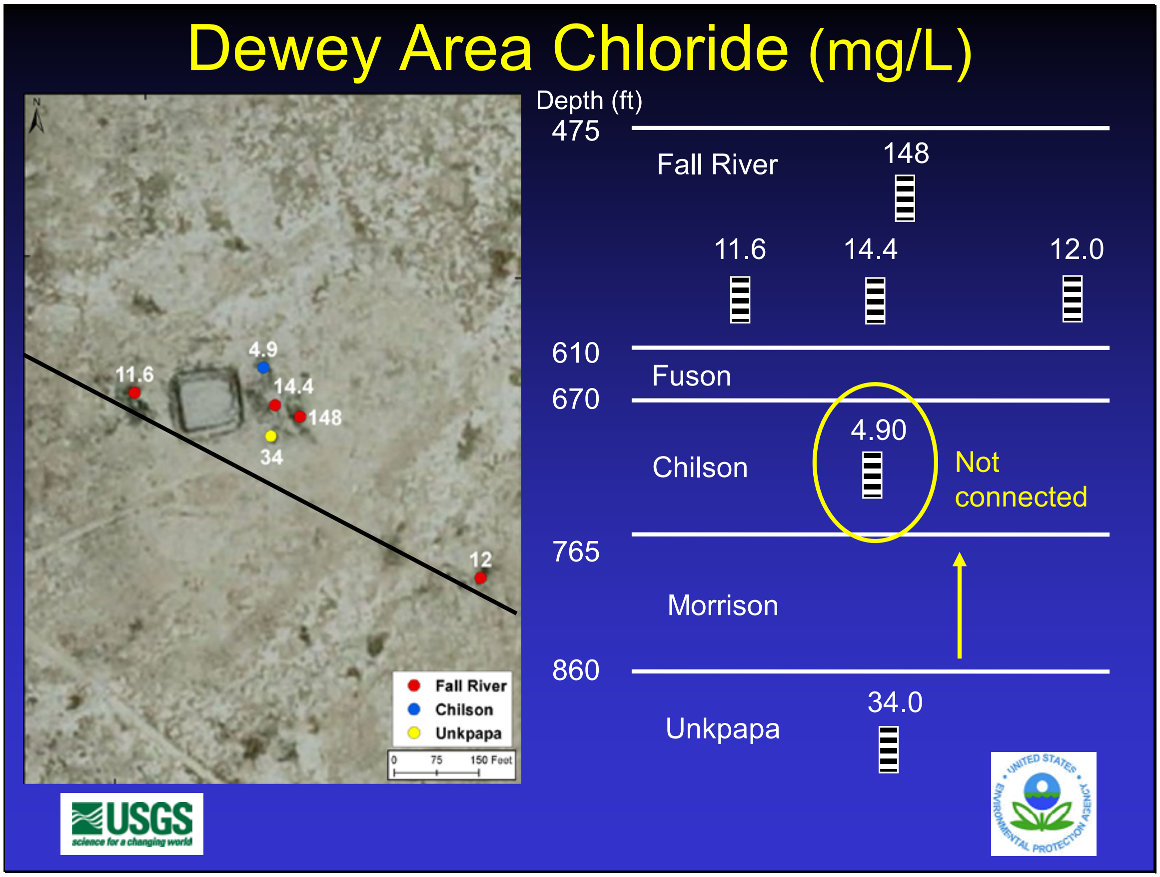
- Conservative tracer
- Dissolution of salt (NaCl)
- May increase along a flow path, but should not decrease
- Good tracer for evidence of aquifer connections
- Detection limit of 1.0 mg/L

Slide 24



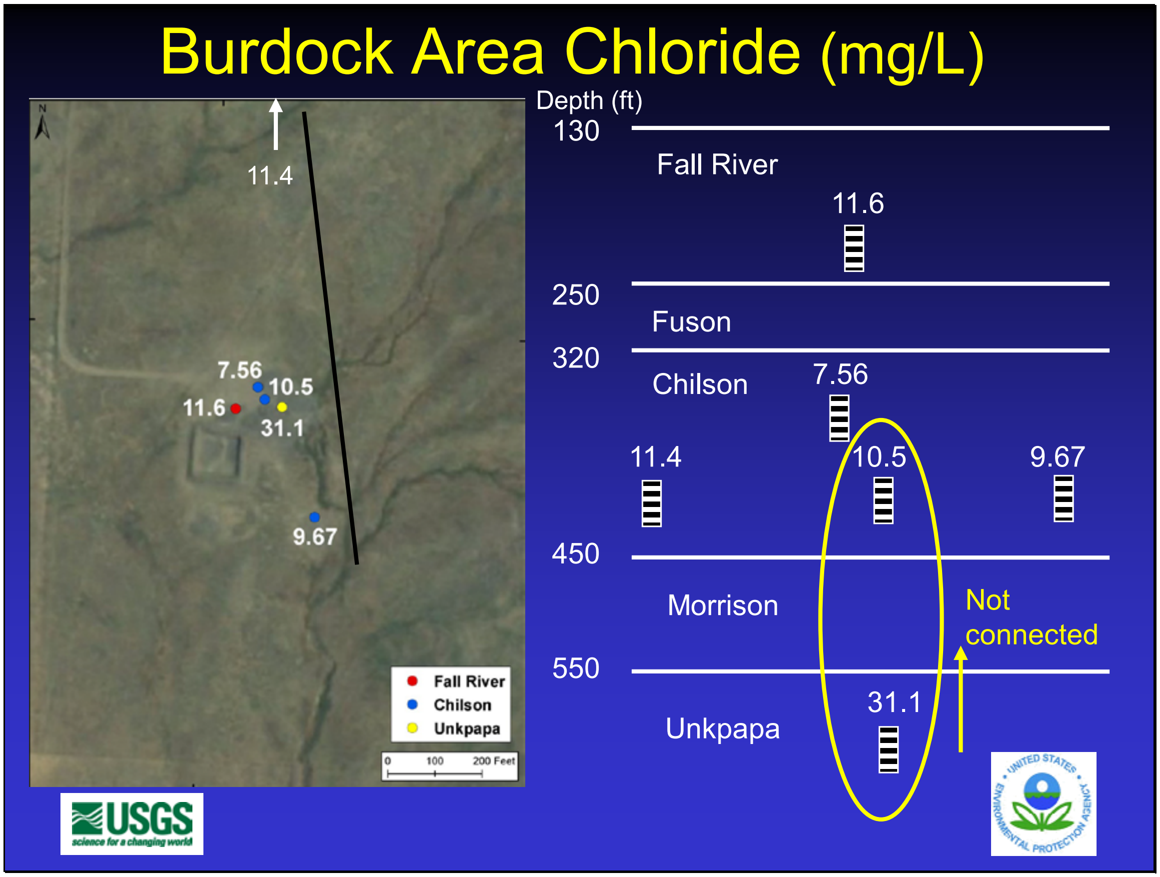
Black rectangles indicate alluvial aquifer wells that probably contact shales that have a higher chloride content.

Slide 25



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

Slide 26



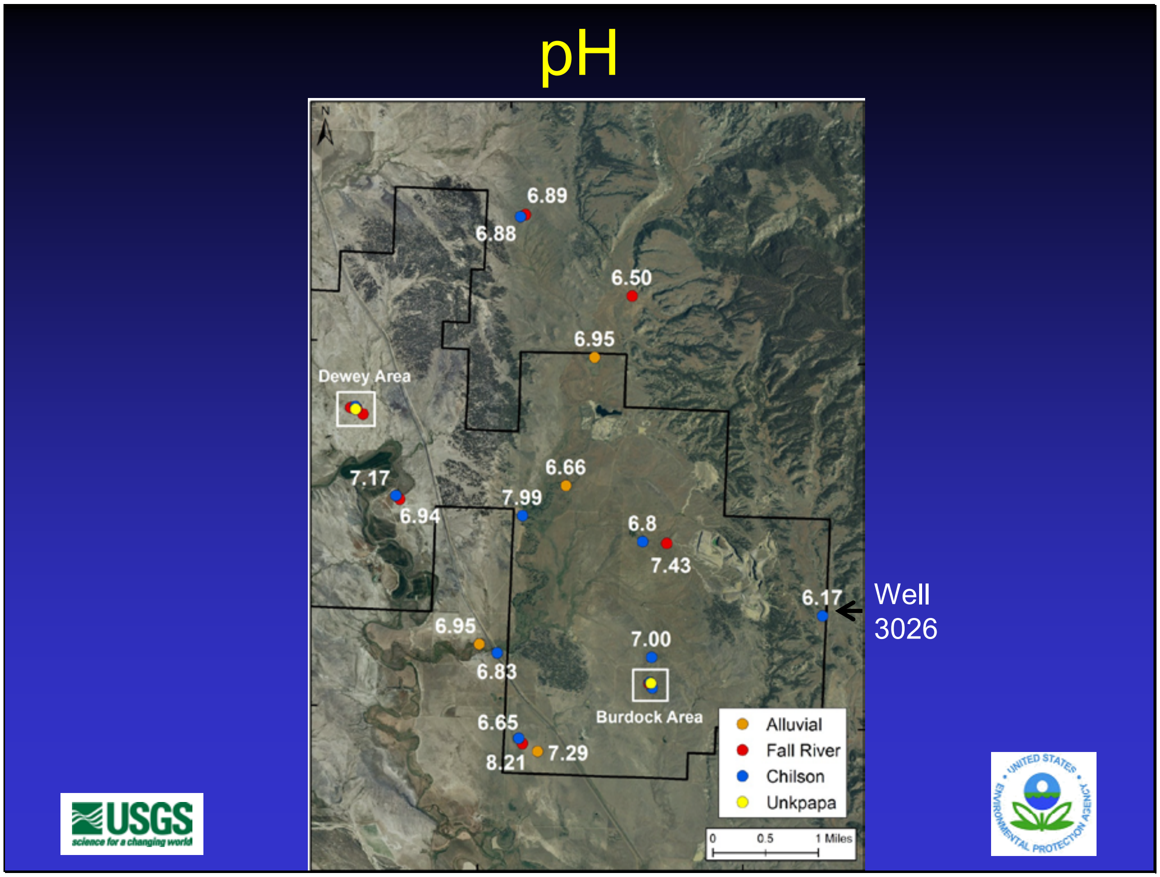
If groundwater flow was significant in the upward direction, chloride would not decrease.

Slide 27

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

Slide 28


pH
6.89
6.88
6.50
6.95
Dewey Area
6.66
7.17
7.99
6.94
6.8
7.43
6.17
Well
3026
6.95
7.00
6.83
Burdock Area
6.65
7.29
8.21
Alluvial
Fall River
Chilson
Unkpapa
0
0.5
1 Miles
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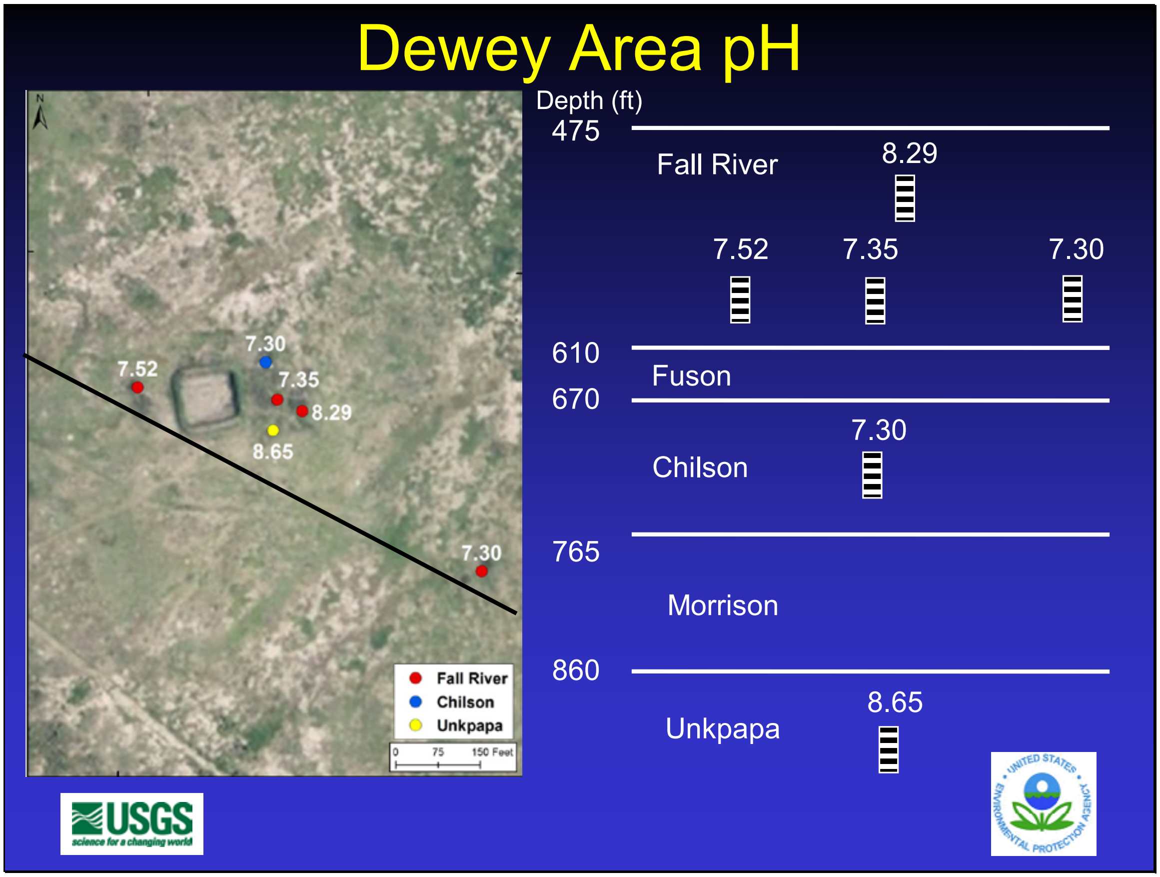
Slide 29



Dewey Area pH
7.30
7.52
7.35
8.29
8.65
7.30
Fall River
Chilson
Unkpapa
0
75
150 Feet
Depth (ft)
475
Fall River
8.29
7.52
7.35
7.30
610
Fuson
670
7.30
Chilson
765
Morrison
860
8.65
Unkpapa
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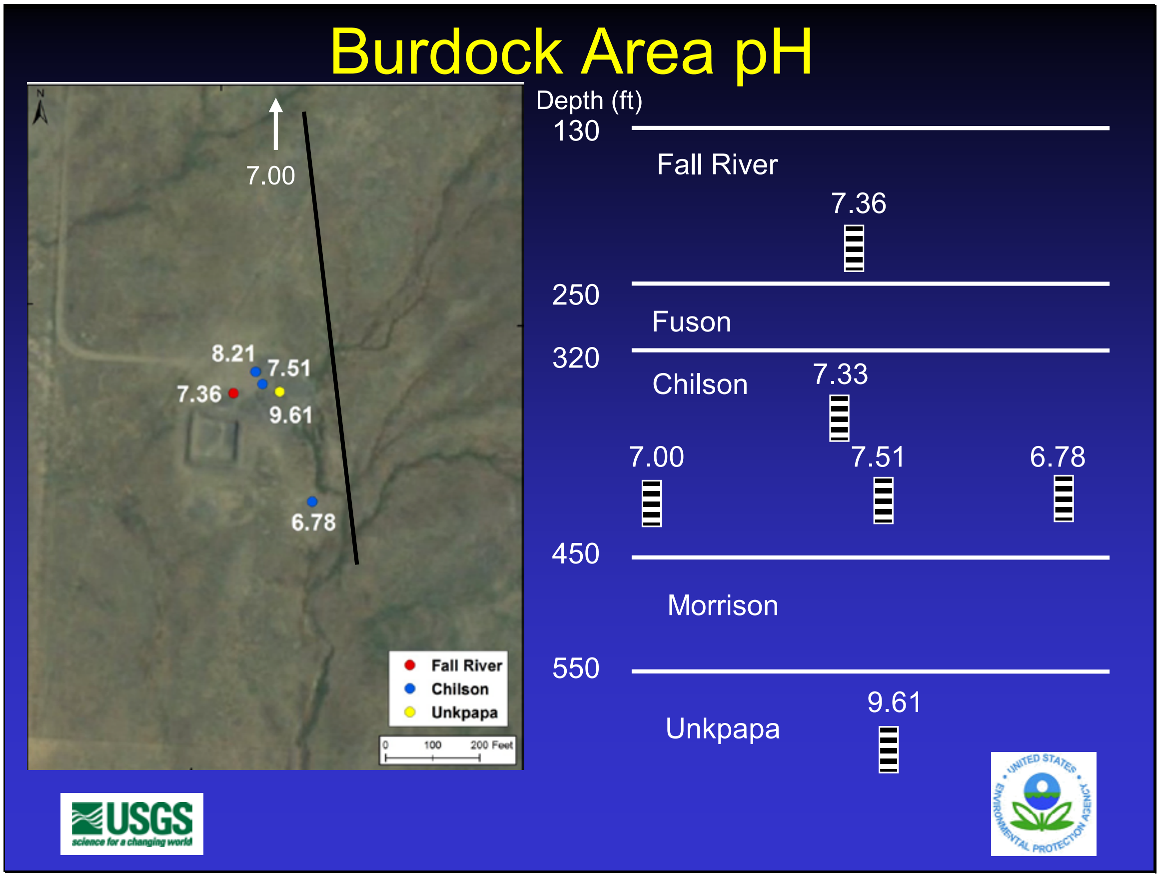
Slide 30



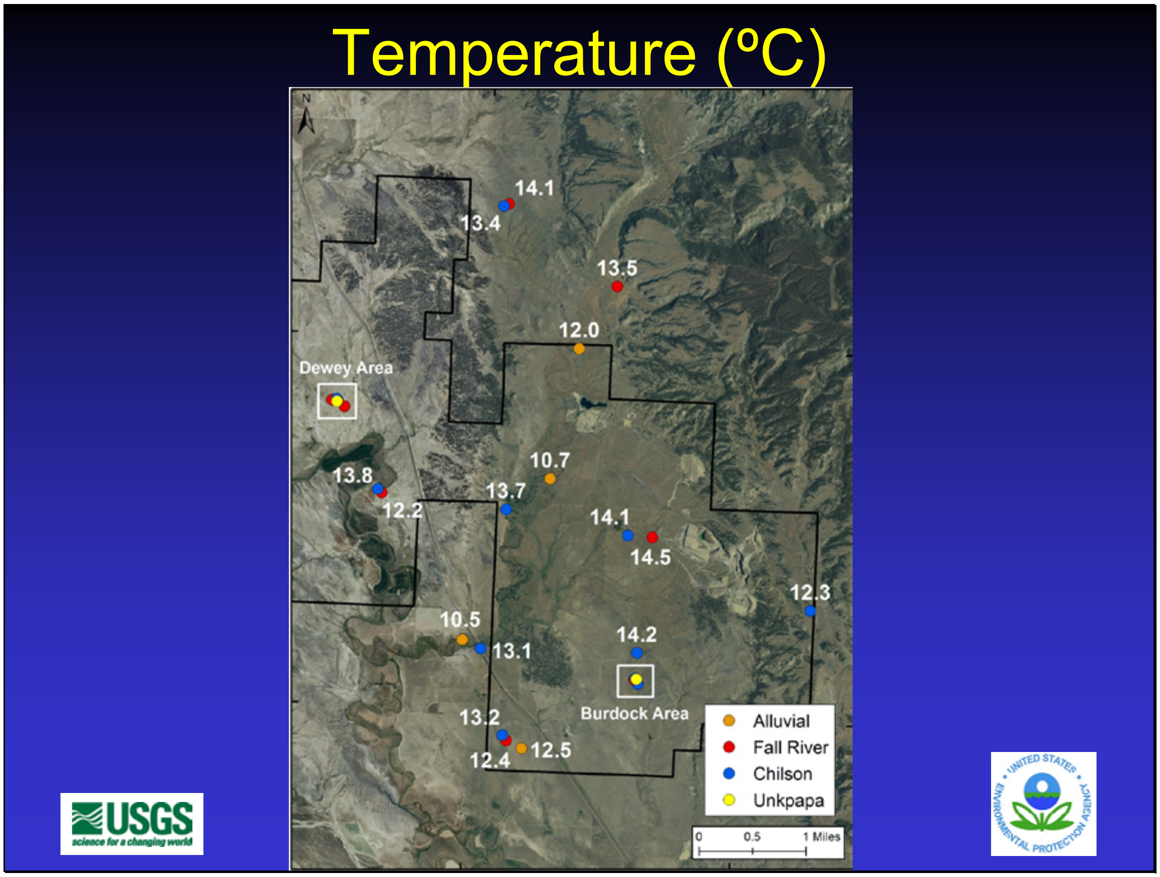
Burdock Area pH
7.00
8.21
7.51
7.36
9.61
6.78
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
7.36
250
Fuson
320
Chilson
7.33
7.00
7.51
6.78
450
Morrison
550
Unkpapa
9.61

Slide 31

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

Slide 32



Temperature (ºC)
14.1
13.4
13.5
12.0
Dewey Area
10.7
13.8
13.7
12.2
14.1
14.5
12.3
10.5
13.1
14.2
Burdock Area
13.2
12.5
12.4
Alluvial
Fall River
Chilson
Unkpapa
0
0.5
1 Miles
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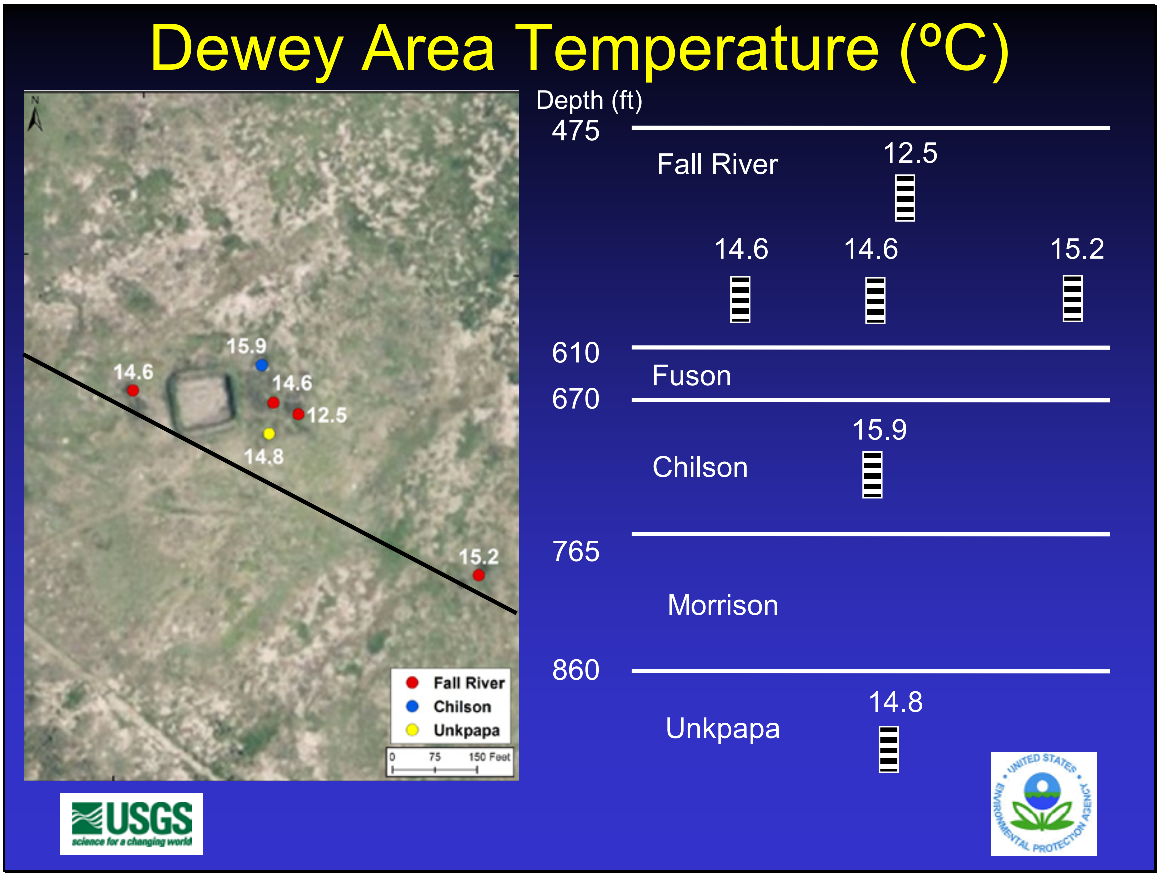
Slide 33



Dewey Area Temperature (ºC)
15.9
14.6
14.6
12.5
14.8
15.2
Fall River
Chilson
Unkpapa
0 75 150 Feet
Depth (ft)
475
Fall River
12.5
14.6
14.6
15.2
610
Fuson
670
Chilson
15.9
765
Morrison
860
Unkpapa
14.8
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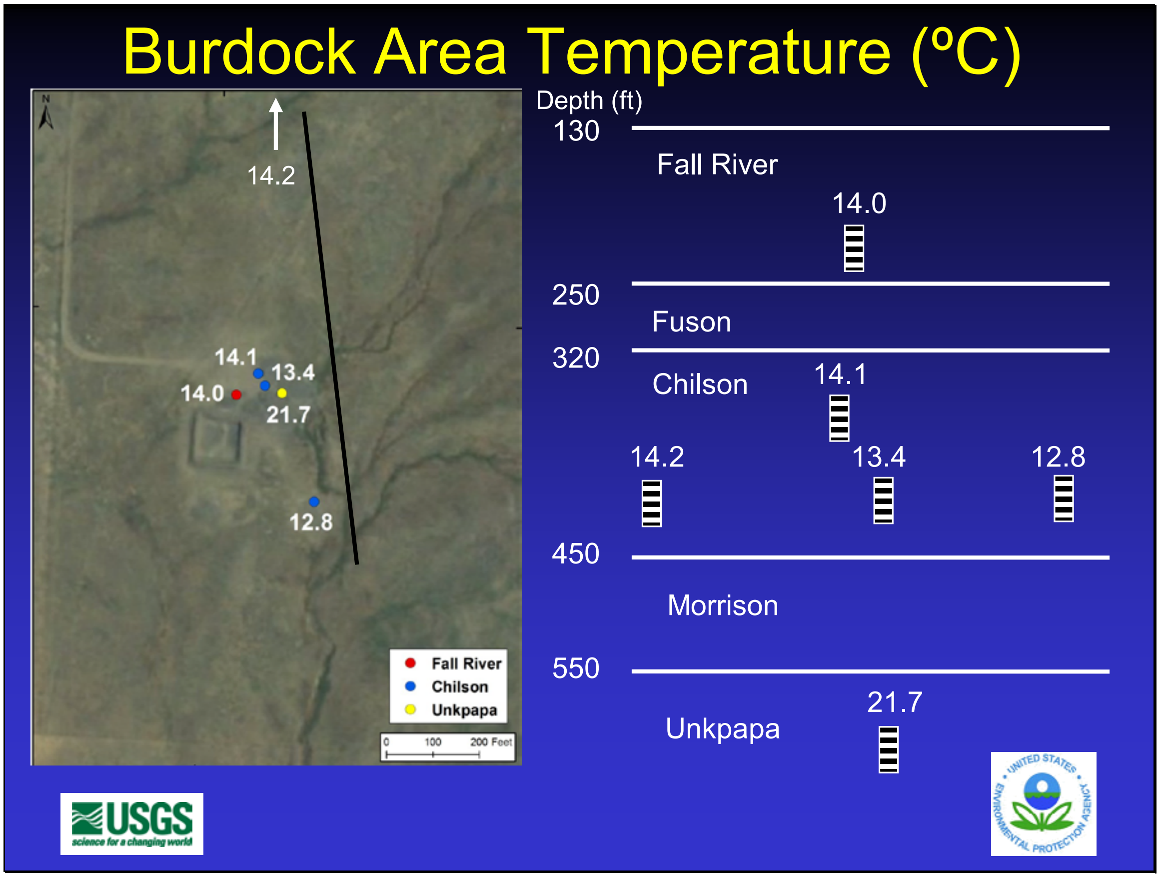
Slide 34

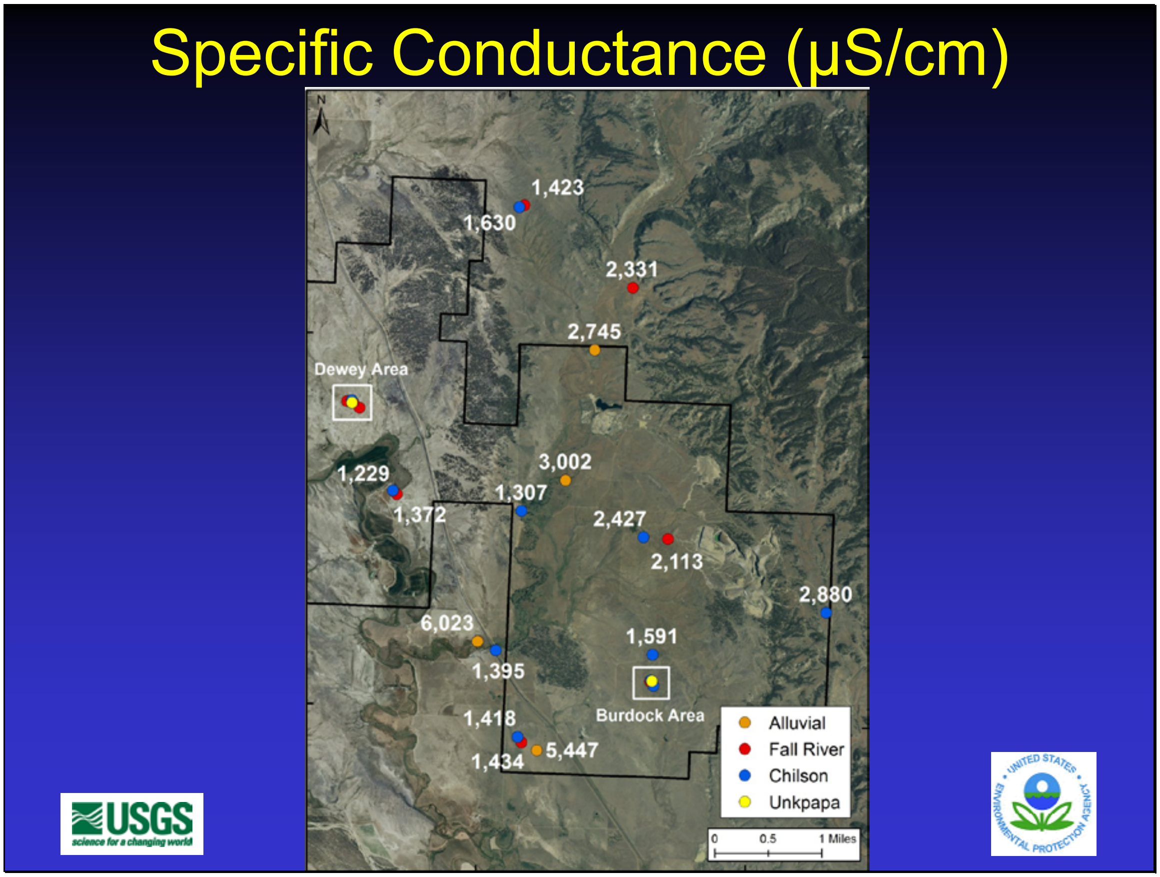


Unkpapa well was very slow flowing and water probably warmed up in the sample tubing.

Specific Conductance

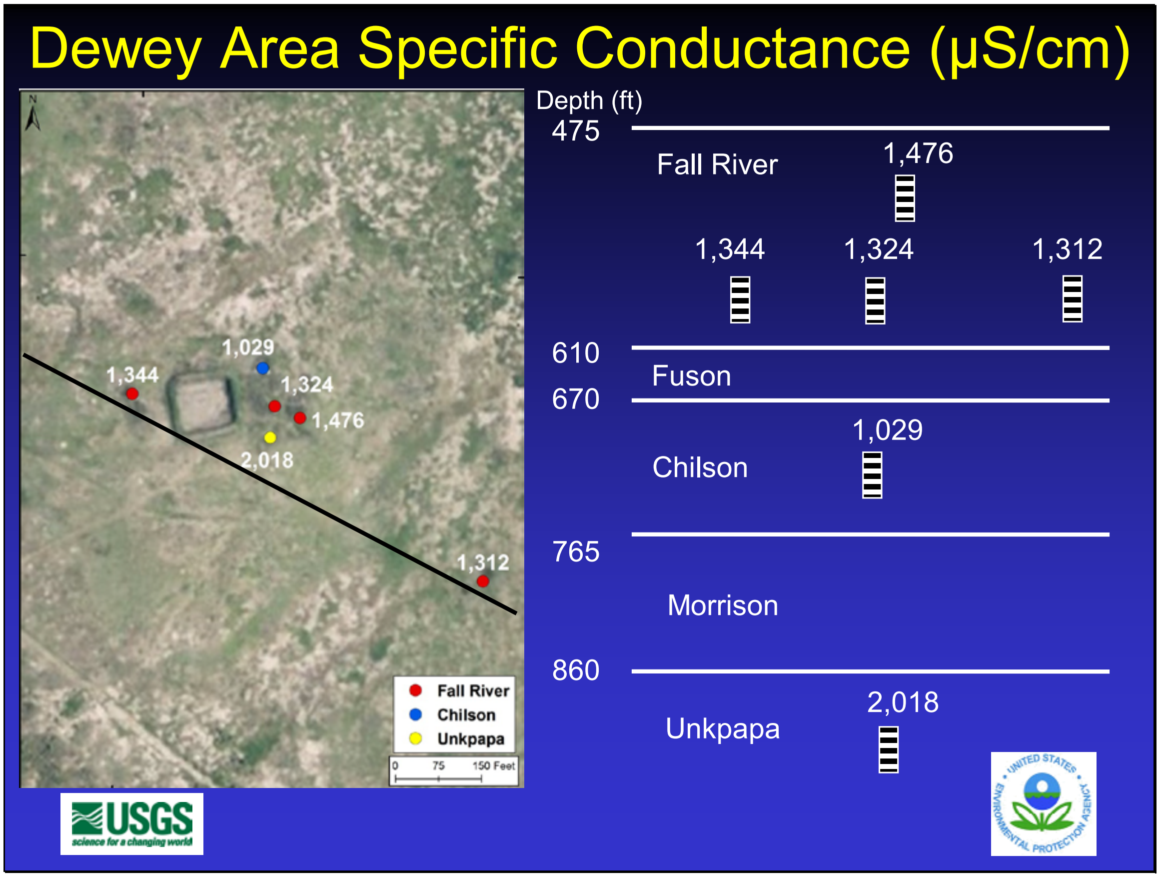
- Easily measured with a handheld meter
- Indicates overall concentration of dissolved constituents
- Does not indicate any particular consituent

Slide 36



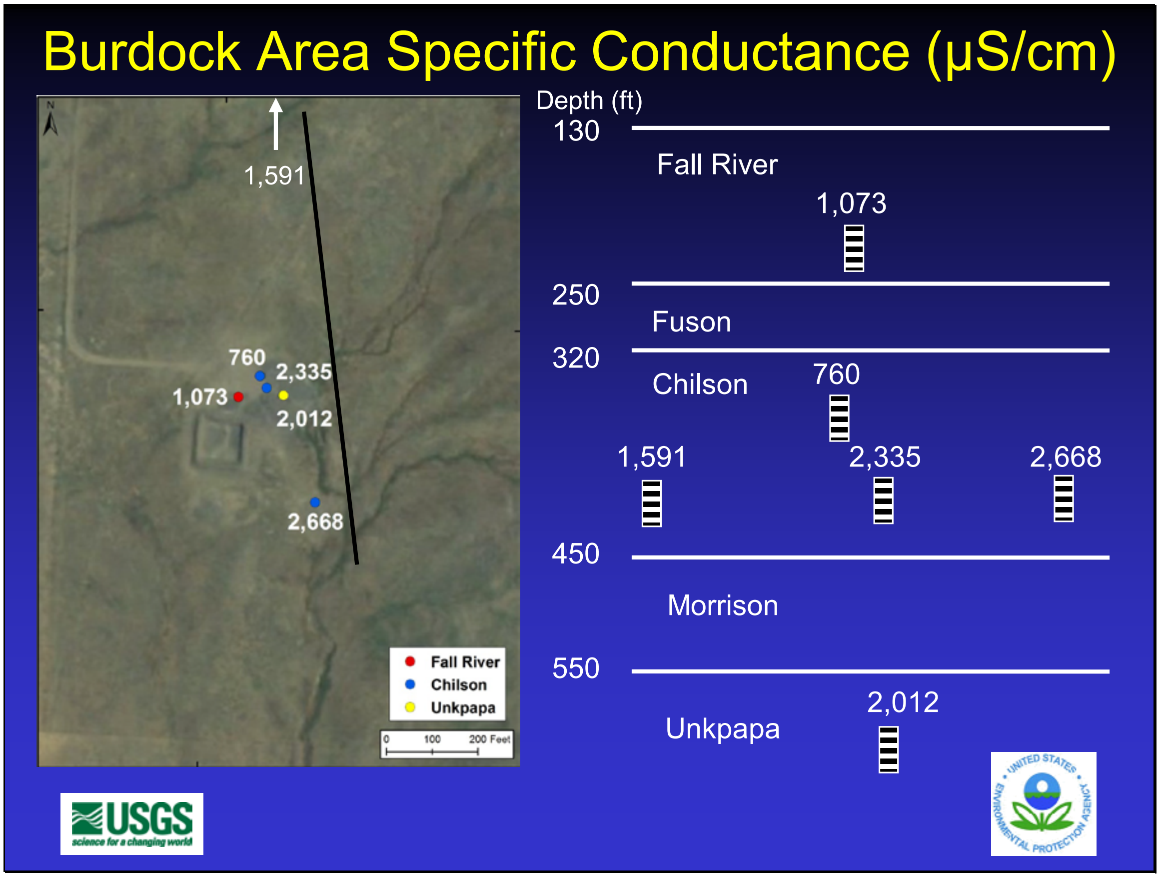
Overall, higher specific conductance in shallow alluvial wells that contact or are near underlying shales.

Slide 37



Dewey Area Specific Conductance (µS/cm)
1,029
1,344
1,324
1,476
2,018
1,312
Fall River
Chilson
Unkpapa
0
75
150 Feet
Depth (ft)
475
Fall River
1,476
1,344
1,324
1,312
610
Fuson
670
1,029
Chilson
765
Morrison
860
2,018
Unkpapa

Slide 38



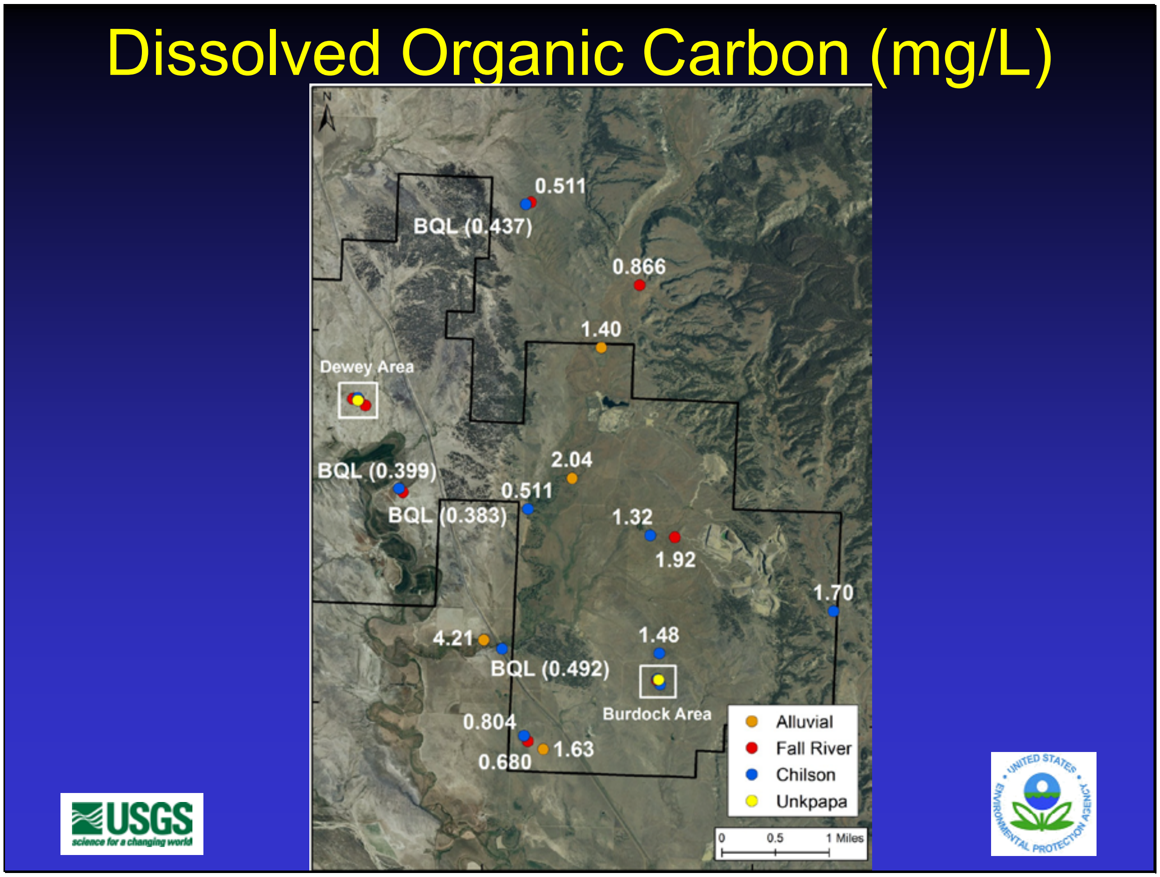
Burdock Area Specific Conductance (µS/cm)
1,591
760
2,335
1,073
2,012
2,668
Fall River
Chilson
Unkpapa
0 100 200 Feet
Depth (ft)
130
Fall River
1,073
250
Fuson
320
Chilson
760
1,591
2,335
2,668
450
Morrison
550
Unkpapa
2,012

Slide 39

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)

Slide 40


Dissolved Organic Carbon (mg/L)
0.511
BQL (0.437)
0.866
1.40
Dewey Area
2.04
BQL (0.399)
0.511
BQL (0.383)
1.32
1.92
1.70
4.21
1.48
BQL (0.492)
Burdock Area
0.804
1.63
0.680
Alluvial
Fall River
Chilson
Unkpapa
0
0.5
1 Miles
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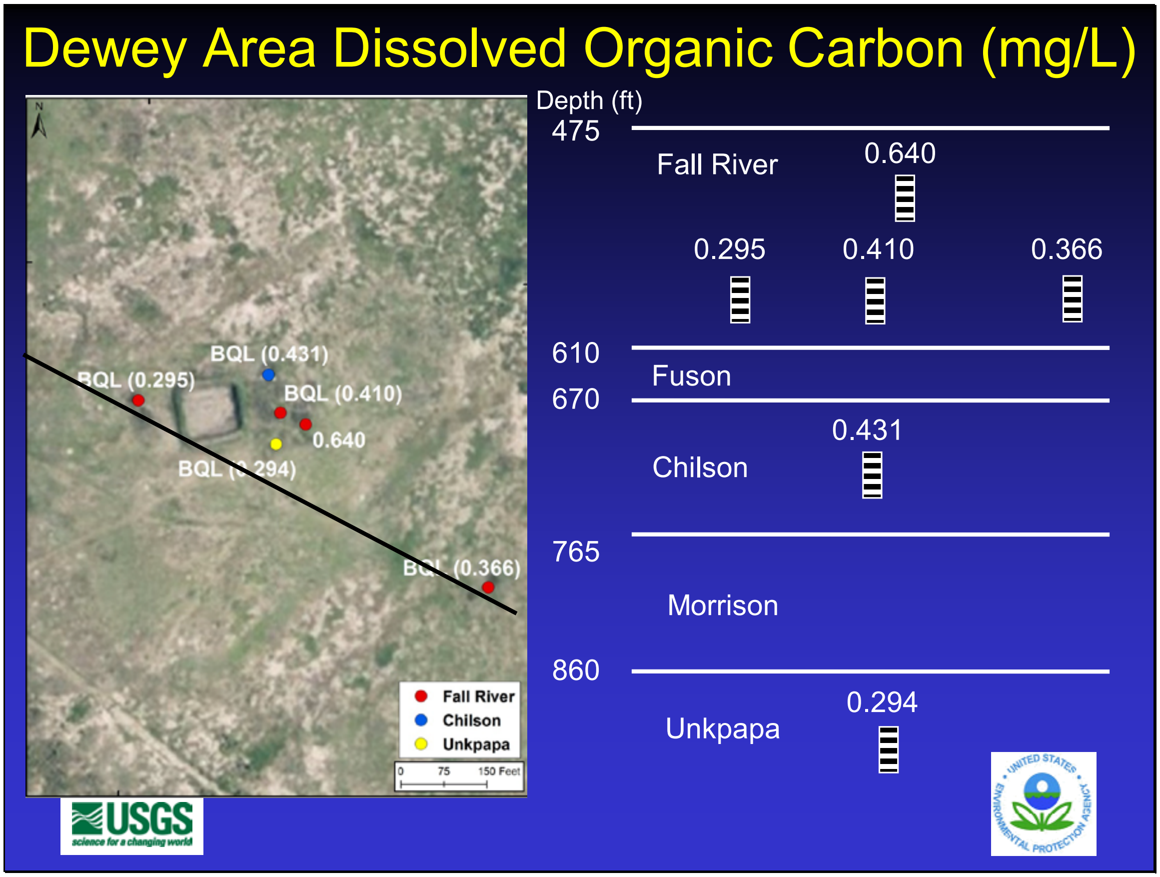

Dewey Area Dissolved Organic Carbon (mg/L)
BQL (0.431)
BQL (0.295)
BQL (0.410)
0.640
BQL (0.294)
BQL (0.366)
Fall River
Chilson
Unkpapa
0 75 150 Feet
Depth (ft)
475
Fall River
0.640
0.295
0.410
0.366
610
Fuson
670
Chilson
0.431
765
Morrison
860
Unkpapa
0.294
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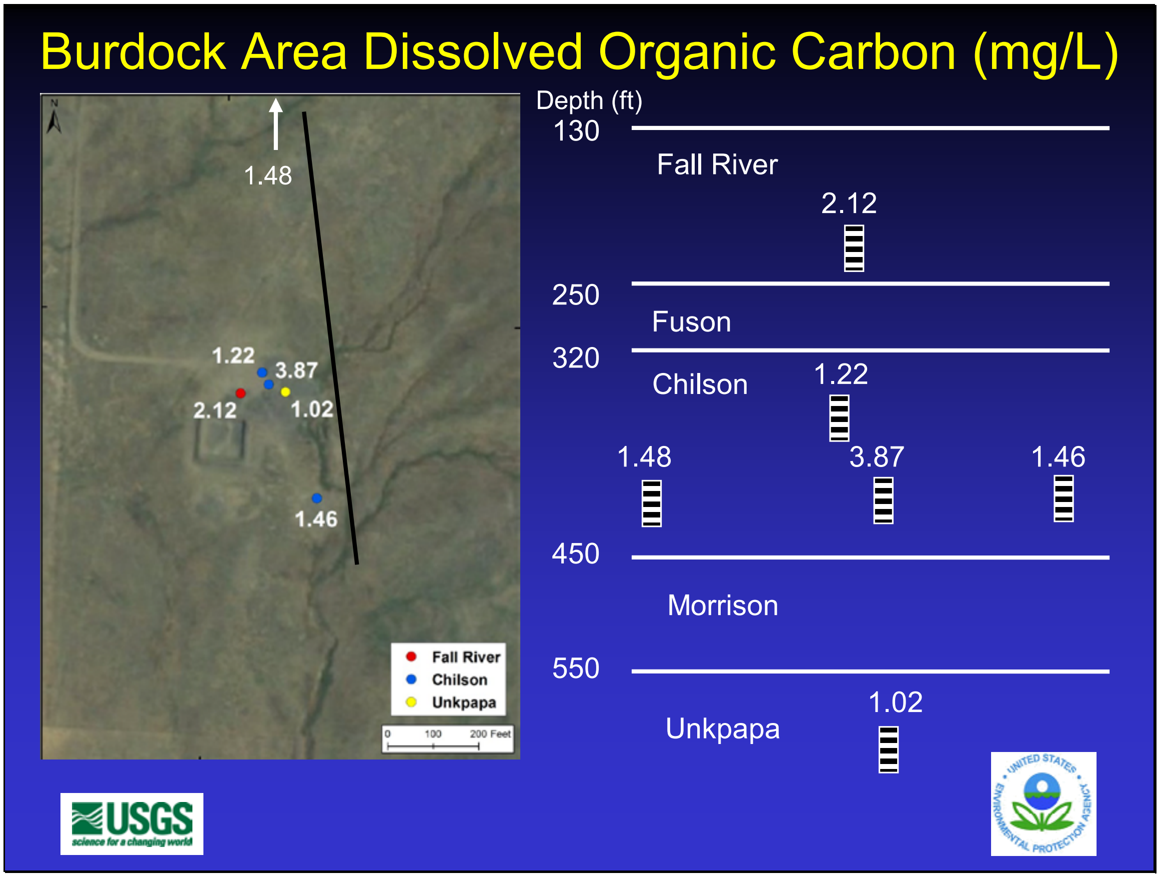
Slide 42



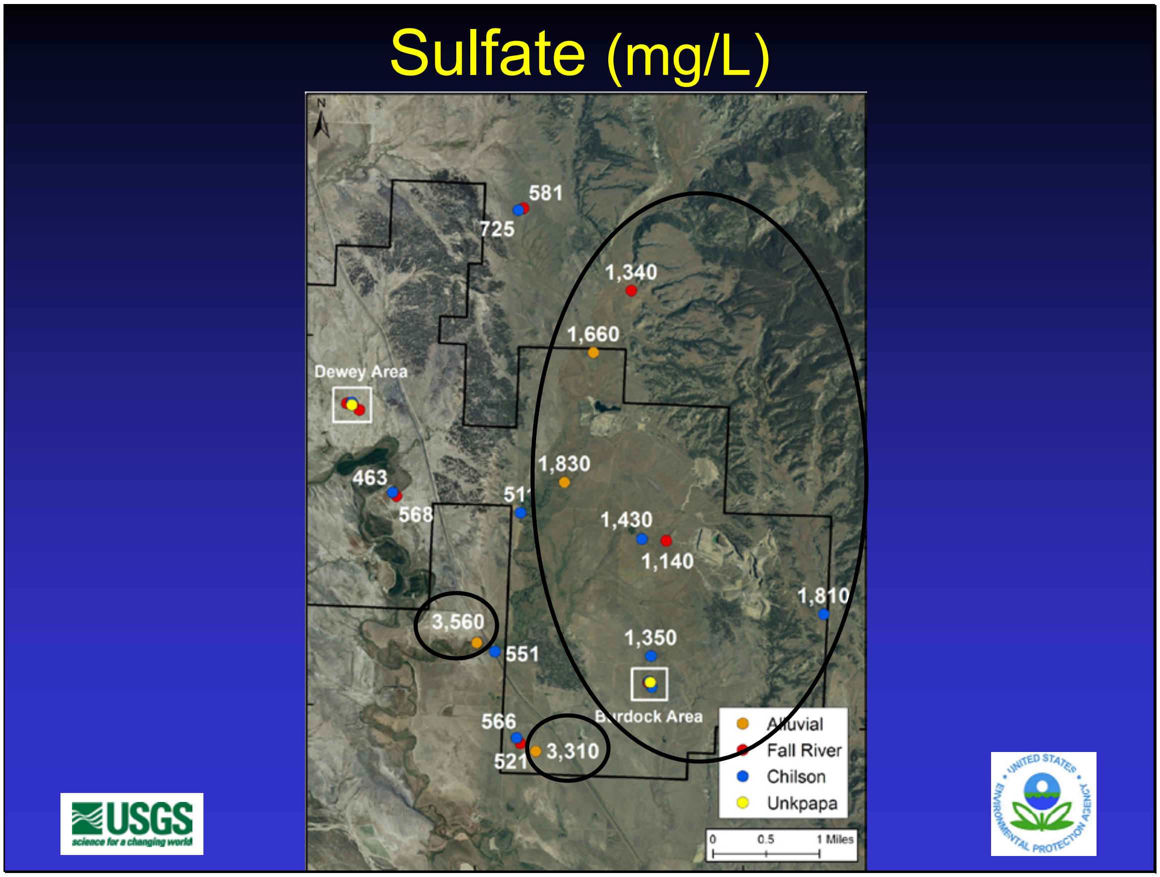
Burdock Area Dissolved Organic Carbon (mg/L)
1.48
1.22
3.87
2.12
1.02
1.46
Fall River
Chilson
Unkpapa
0 100 200 Feet
Depth (ft)
130
Fall River
2.12
250
Fuson
320
Chilson
1.22
1.48
3.87
1.46
450
Morrison
550
Unkpapa
1.02

Slide 43

^{34}S and Sulfate

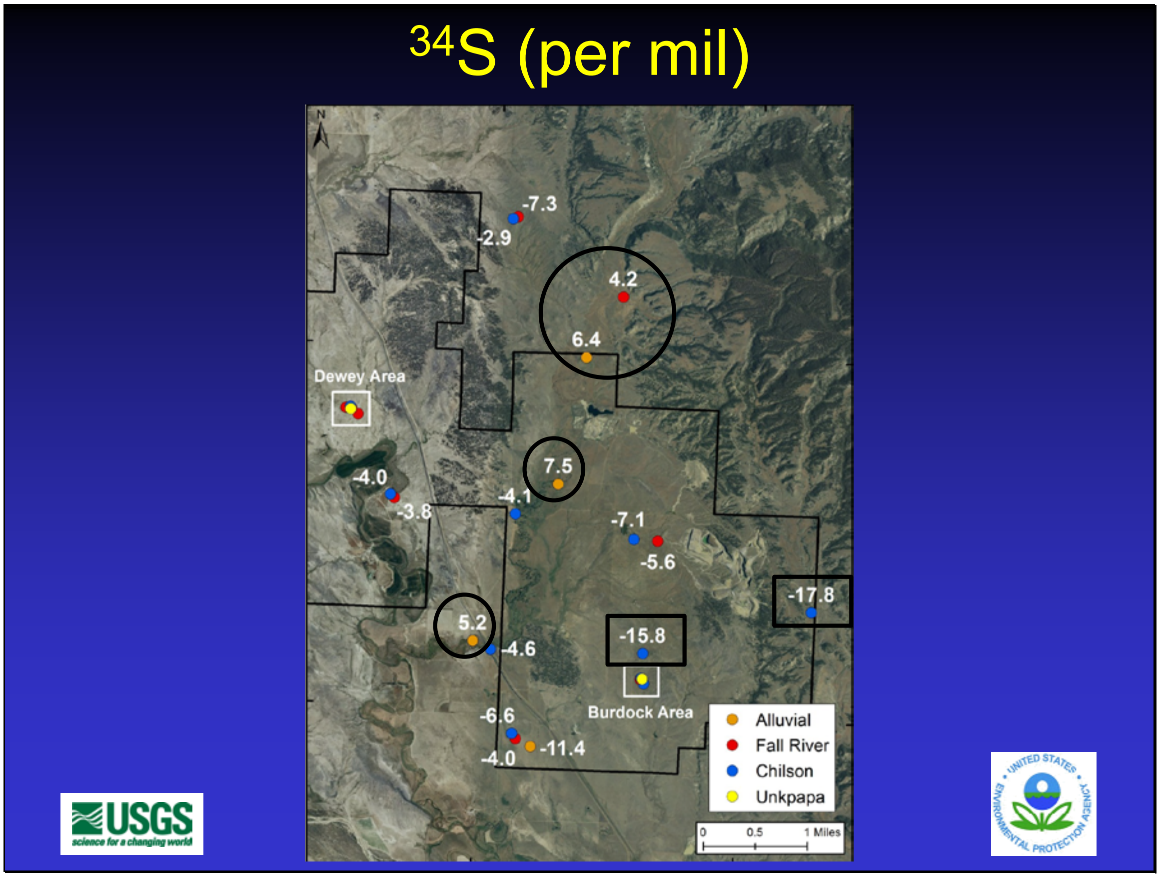
- Sulfur is in solution as sulfate
- Sulfate source is either
  - Gypsum or anhydrite ($CaSO_4$) – positive ^{34}S value
  - Sulfide oxidation – negative ^{34}S value
- Intermediate ^{34}S values = mixed source
- Dewey area – some additional sulfate dissolution is possible (slightly undersaturated for 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}S and detection limit for sulfate of 1 mg/L

Slide 44



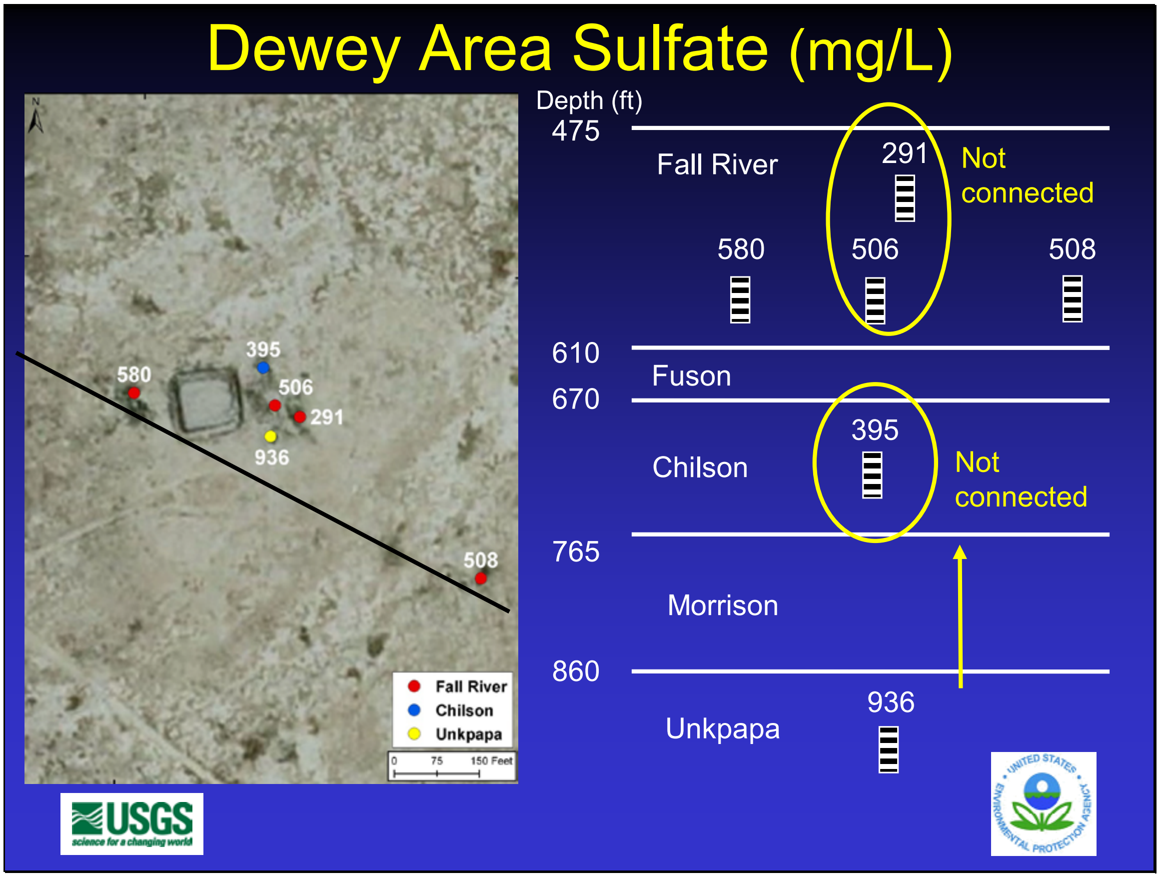
Large circle indicates Burdock area with sulfate near 1,500 mg/L.
Small circles indicate alluvial wells near shale bedrock and resulting high sulfate concentration. Wells outside of the Burdock area are all near 500-700 mg/L sulfate.

Slide 45



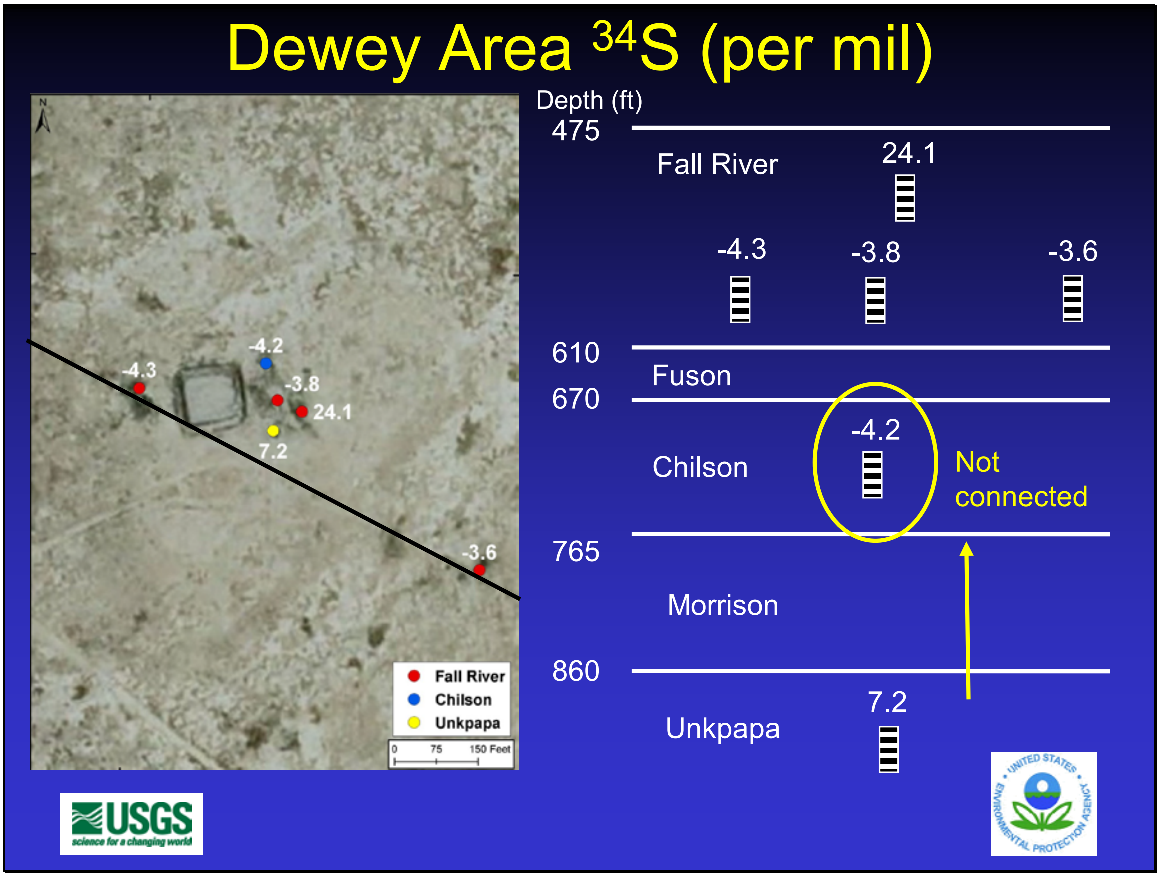
Rectangles indicate wells with more negative values due to sulfide oxidation. Circles indicate wells with more positive values indicative of gypsum dissolution. Intermediate values are likely due to mixing.

Slide 46



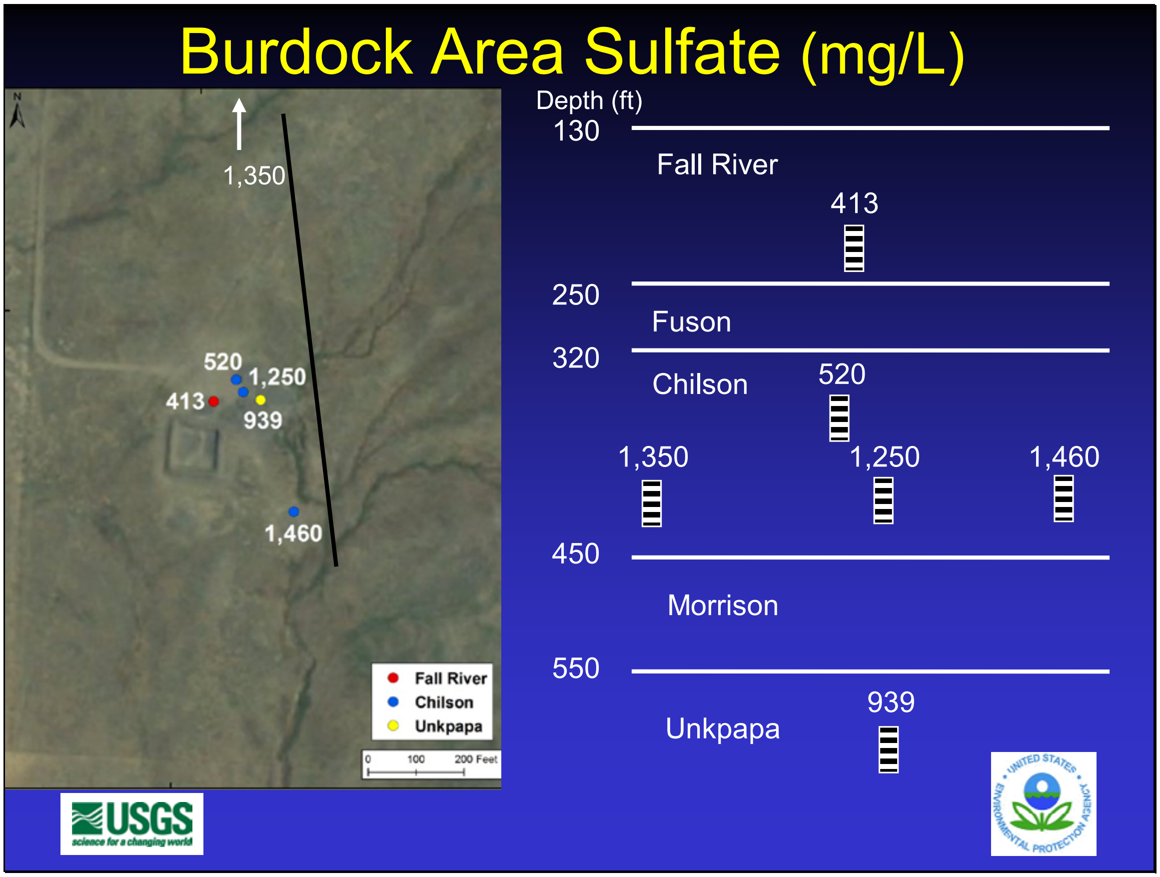
Groundwater connections do not appear likely, as sulfate concentration should only increase with more gypsum dissolution. Groundwater conditions are not known to be sulfate reducing (which would remove sulfate).

Slide 47



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.

Slide 48


Burdock Area Sulfate (mg/L)
1,350
520
1,250
413
939
1,460
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
413
250
Fuson
320
Chilson
520
1,350
1,250
1,460
450
Morrison
550
Unkpapa
939
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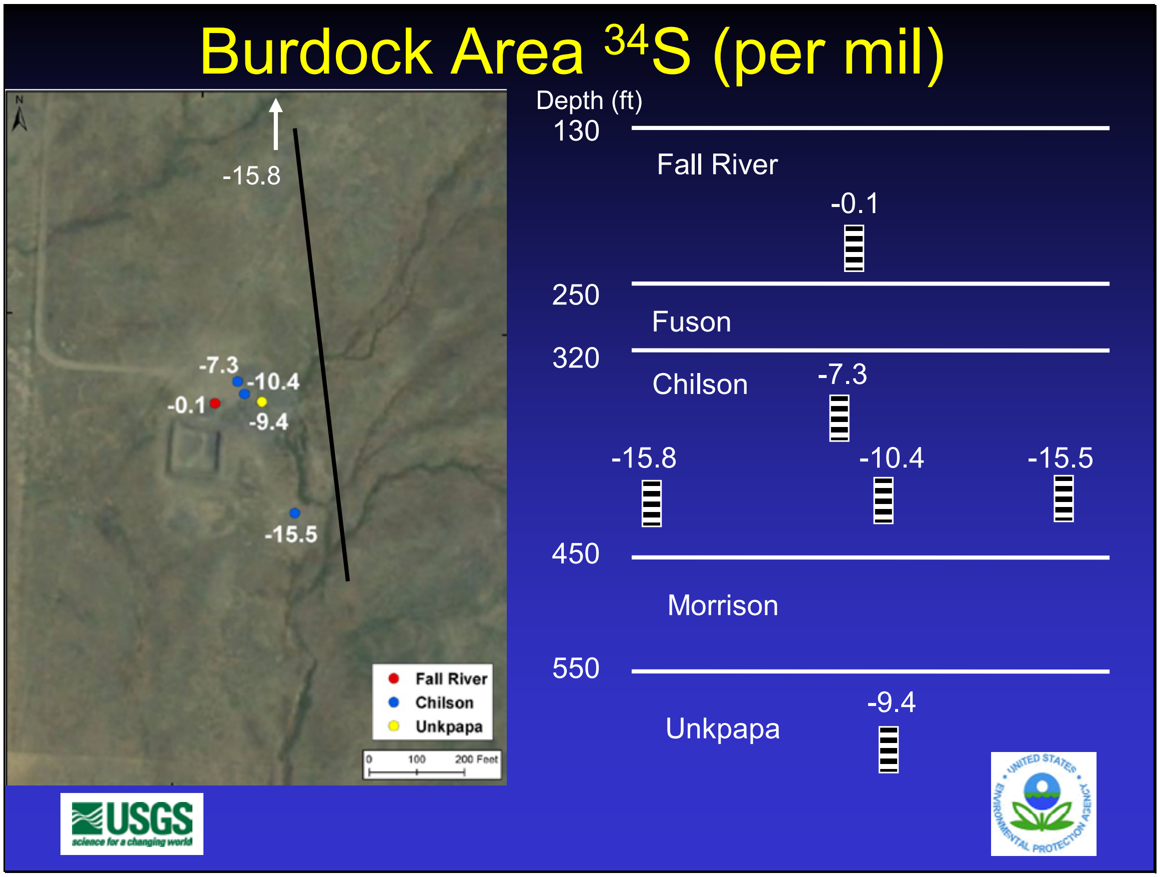
Slide 49



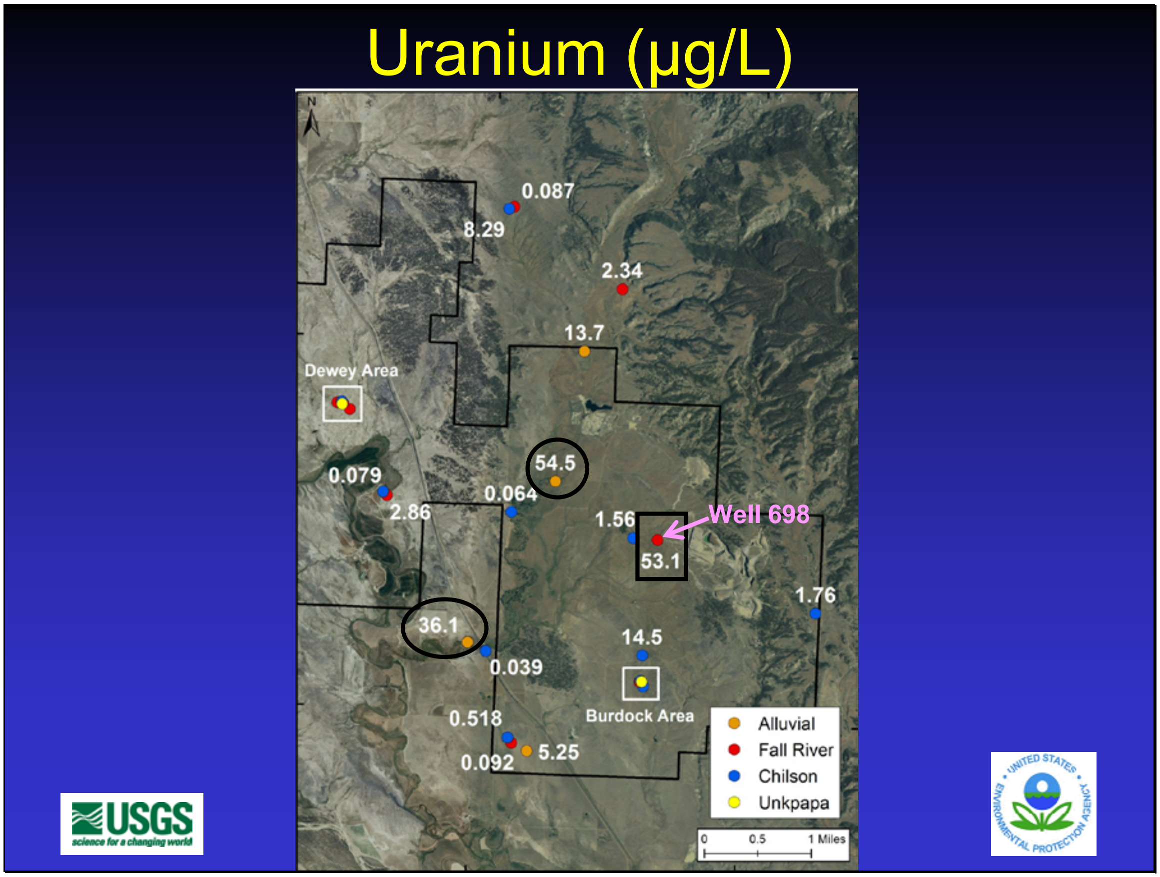
Burdock Area ^{34}S (per mil)
-15.8
-7.3
-10.4
-0.1
-9.4
-15.5
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
-0.1
250
Fuson
320
Chilson
-7.3
-15.8
-10.4
-15.5
450
Morrison
550
Unkpapa
-9.4

Slide 50

Uranium

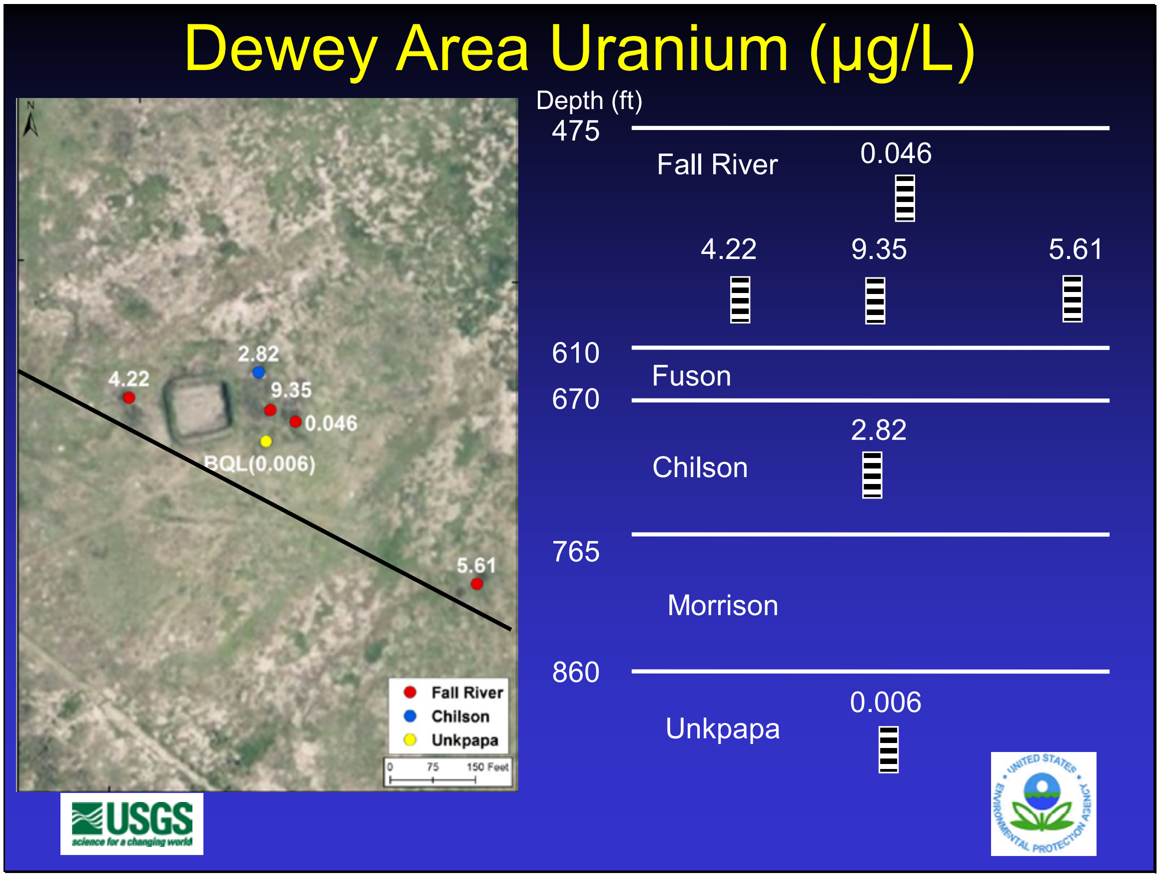
- Uranium is more soluble with oxidizing groundwater
- Uranium concentrations in deep units are all below drinking water standards (reducing conditions)
- Highest uranium is in alluvial wells
- Well 698 suggests that in order to precipitate uranium, contact with reductive solids is necessary beyond having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

Slide 51



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.

Slide 52


Dewey Area Uranium (µg/L)
4.22
2.82
9.35
0.046
BQL(0.006)
5.61
Fall River
Chilson
Unkpapa
0 75 150 Feet
Depth (ft)
475
Fall River
0.046
4.22
9.35
5.61
610
Fuson
670
Chilson
2.82
765
Morrison
860
Unkpapa
0.006
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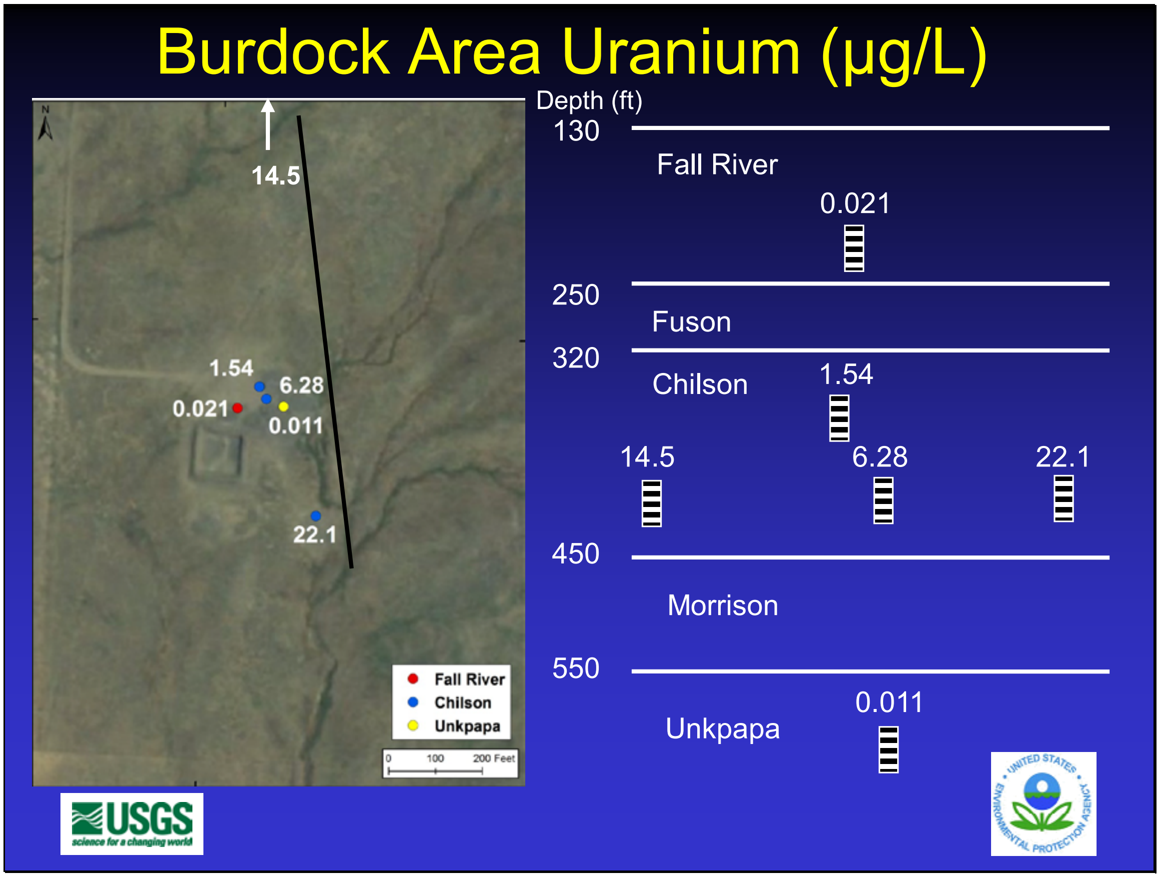
Slide 53



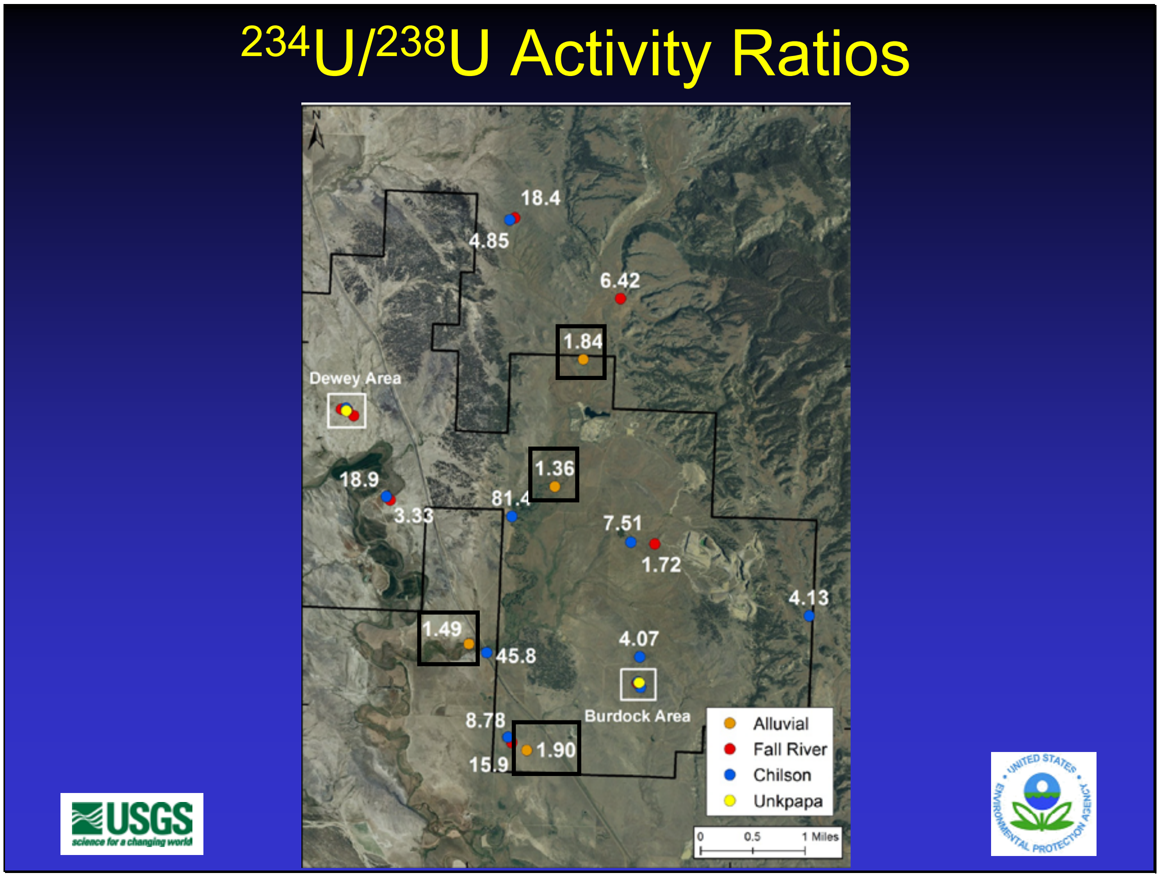
Wells 682 and 684 (14.5 and 22.1 ppb uranium) have some screening in the oxidized zone.
Well 680 (6.28 ppb) is all in the reducing zone.

Slide 54

$^{234}U/^{238}U$ Activity Ratios

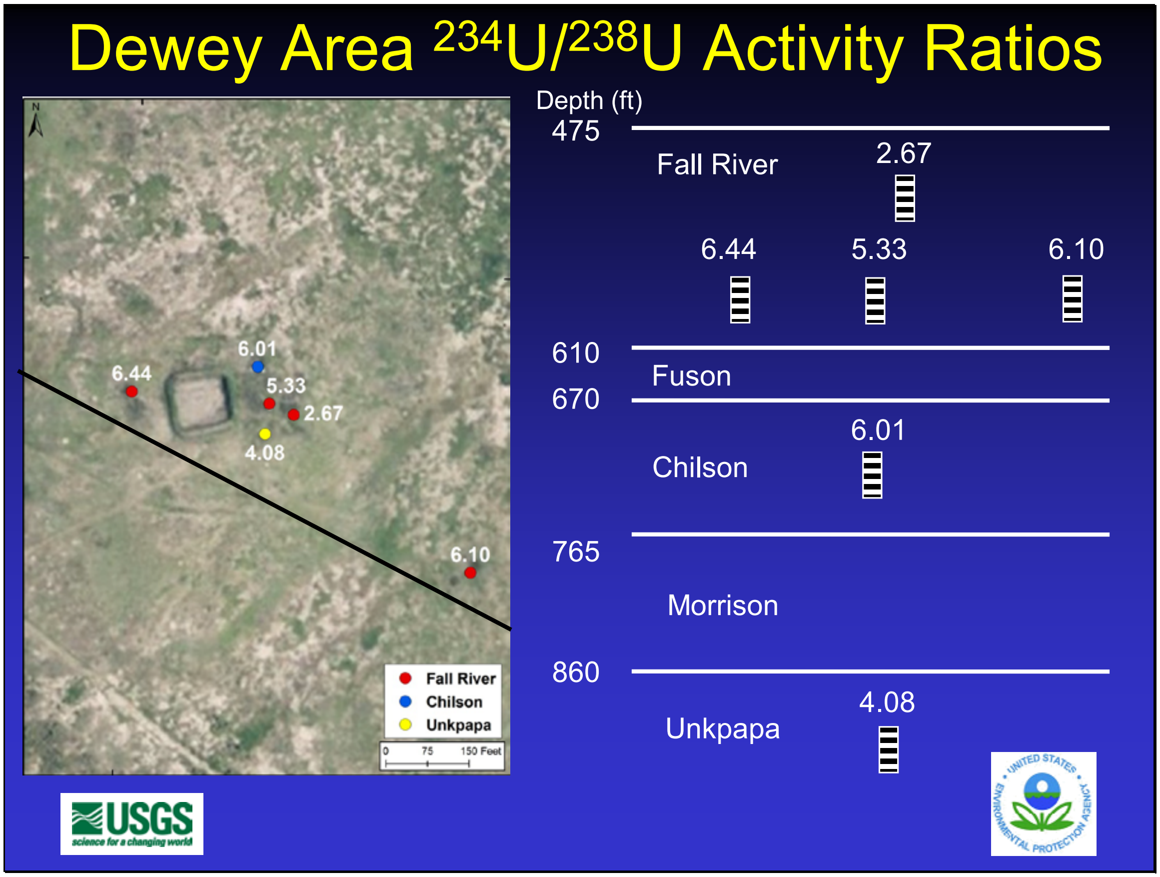
- ^{234}U leaches more readily than ^{238}U
- Higher ratios indicate a slower leaching process
- Values near 1.5 are typical of naturally occurring, young groundwaters

Slide 55



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.

Slide 56


Dewey Area $^{234}U/^{238}U$ Activity Ratios
Depth (ft)
475
Fall River
2.67
6.44
5.33
6.10
610
Fuson
670
6.01
Chilson
765
Morrison
860
4.08
Unkpapa
6.01
6.44
5.33
2.67
4.08
6.10
Fall River
Chilson
Unkpapa
0
75
150 Feet
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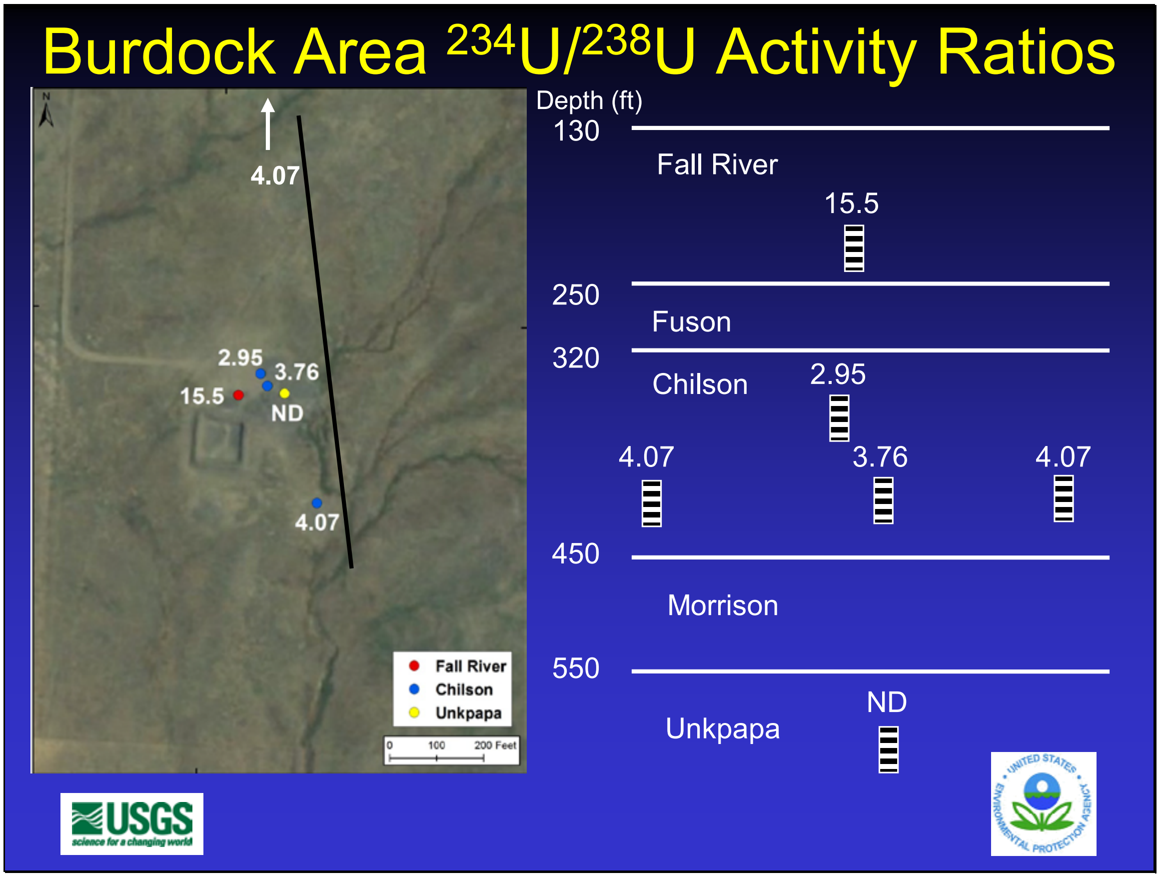
Slide 57



Burdock Area 234U/238U Activity Ratios
N
4.07
2.95
3.76
15.5
ND
4.07
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
15.5
250
Fuson
320
Chilson
2.95
4.07
3.76
4.07
450
Morrison
550
Unkpapa
ND
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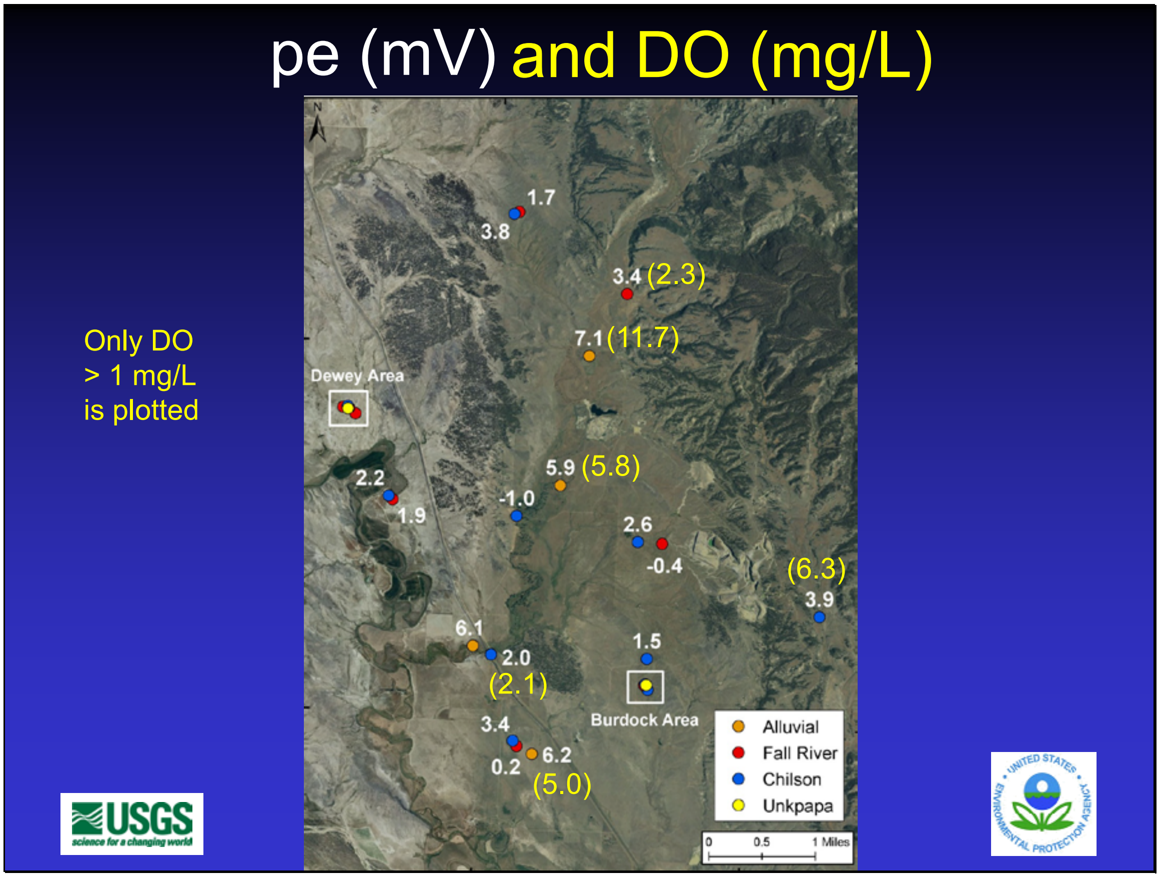
pe and Dissolved Oxygen (DO)

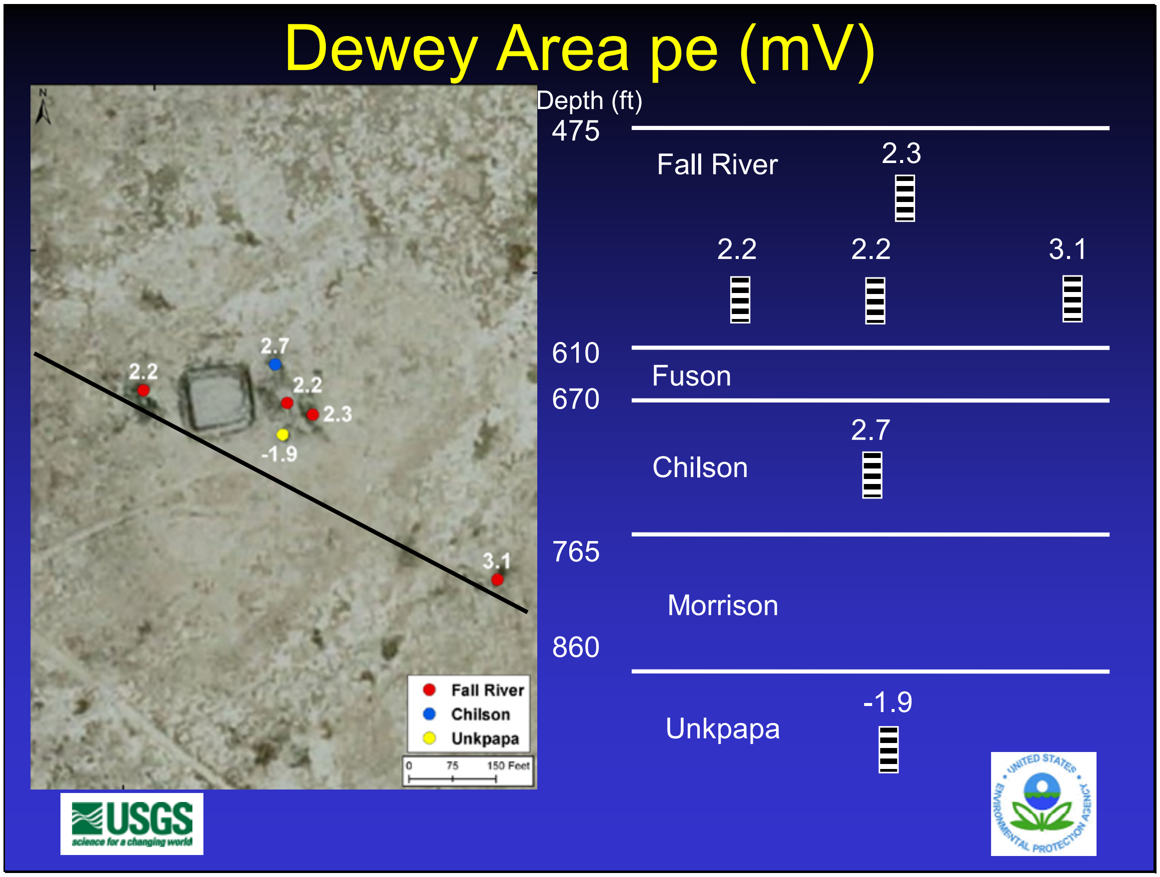
- pe is a measure of the reducing versus oxidizing conditions
- pe is difficult to measure accurately in the field
  - Need a good redox pair
  - Groundwater is not always in redox equilibrium
- DO is also very difficult to measure in the field, especially at lower concentrations
  - Best to use as a 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

Slide 59



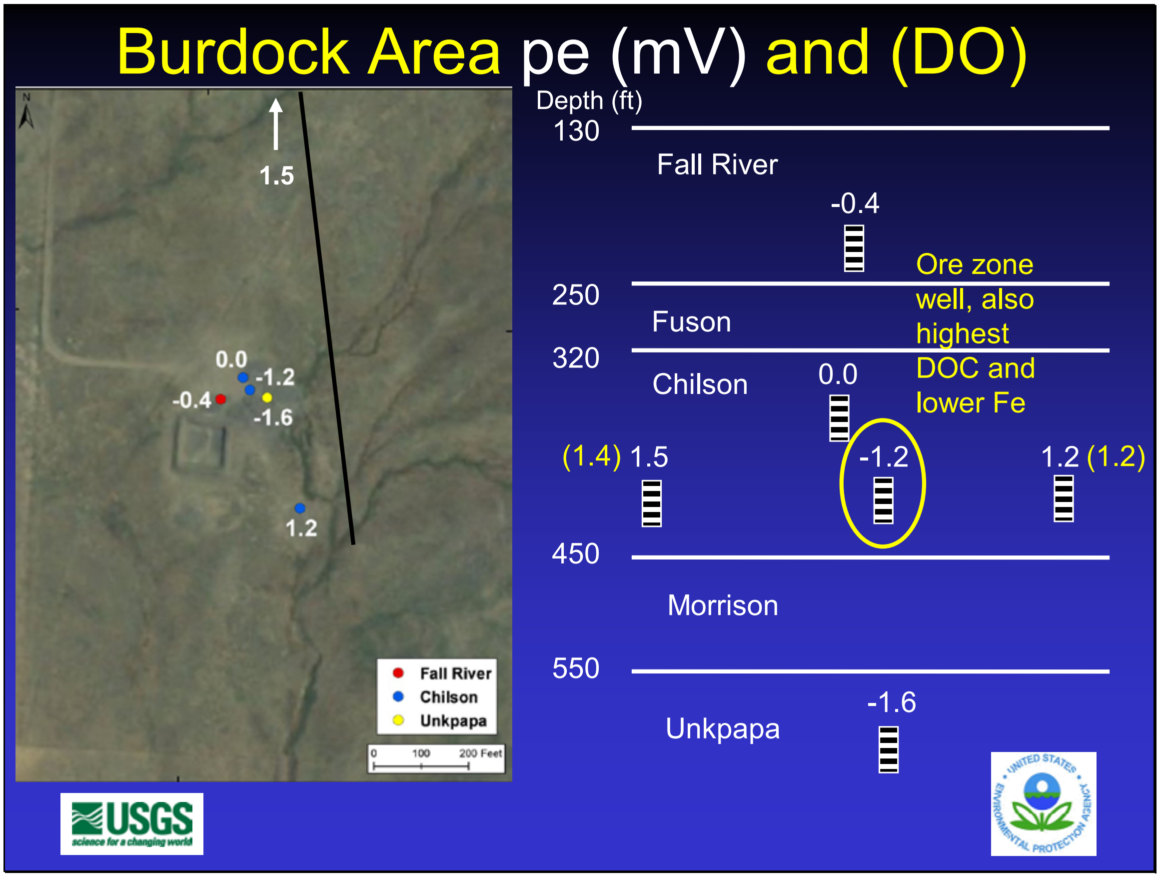
Note that in this slide and subsequent pe/DO slides, ONLY DO that is greater than 1 mg/L is plotted.
DO < 1 mg/L is not quantitatively detectable with the handheld meter than was used.

Slide 60



No DO was detected.

Slide 61

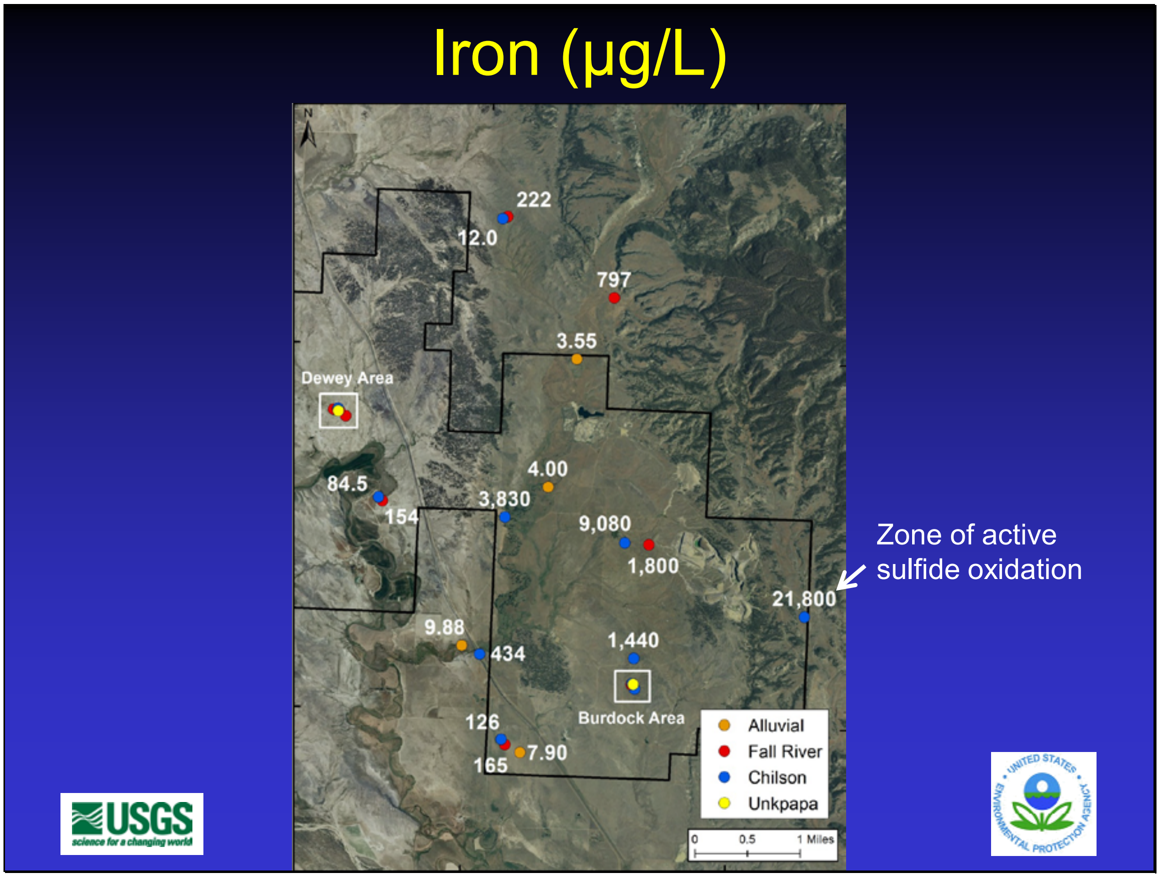


DOC = dissolved organic carbon.
684 and 682 (wells with DO indicated in parentheses) have some screening in oxidized zone, 680 (circled well) is all in reducing solid phase material.
ONLY DO that is greater than 1 mg/L is plotted.

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

Slide 63


Iron (µg/L)
222
12.0
797
3.55
Dewey Area
4.00
84.5
154
3,830
9,080
1,800
21,800
9.88
434
1,440
Burdock Area
126
165
7.90
Alluvial
Fall River
Chilson
Unkpapa
0
0.5
1 Miles
Zone of active sulfide oxidation
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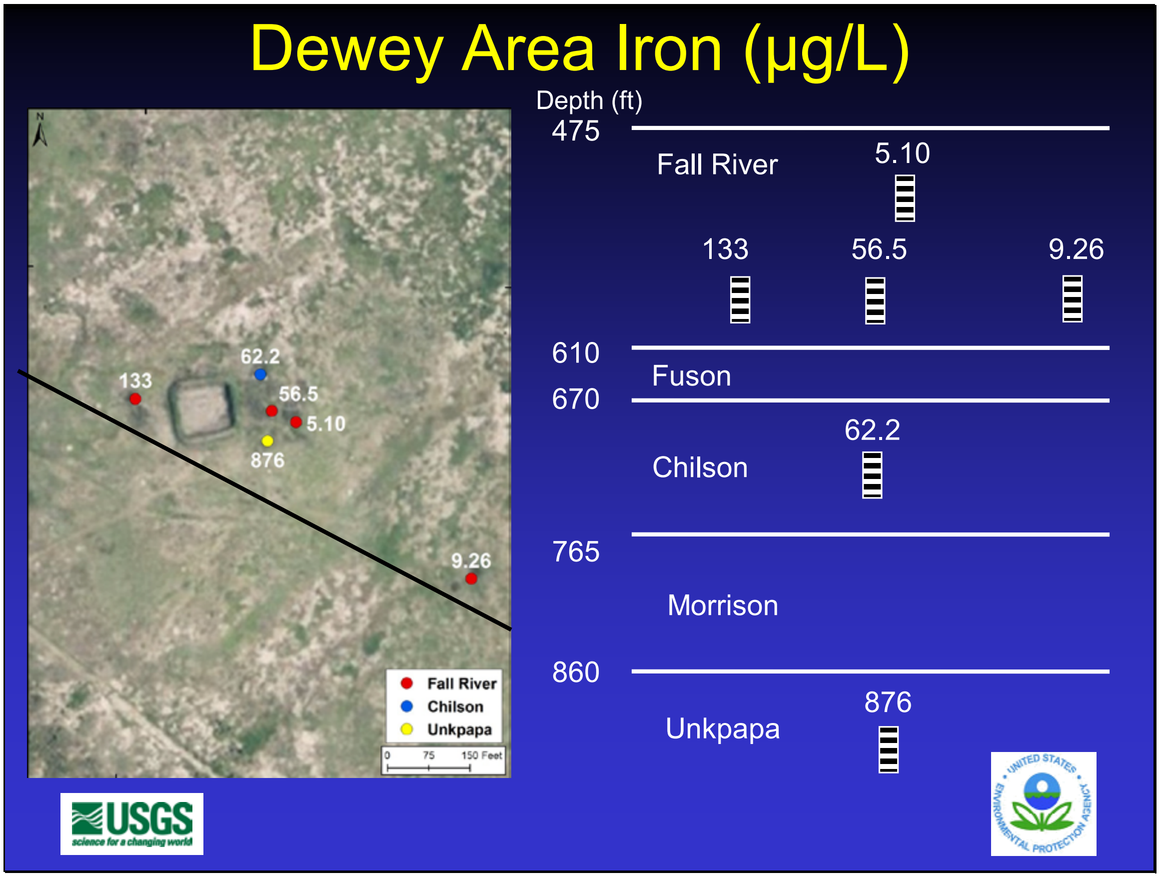
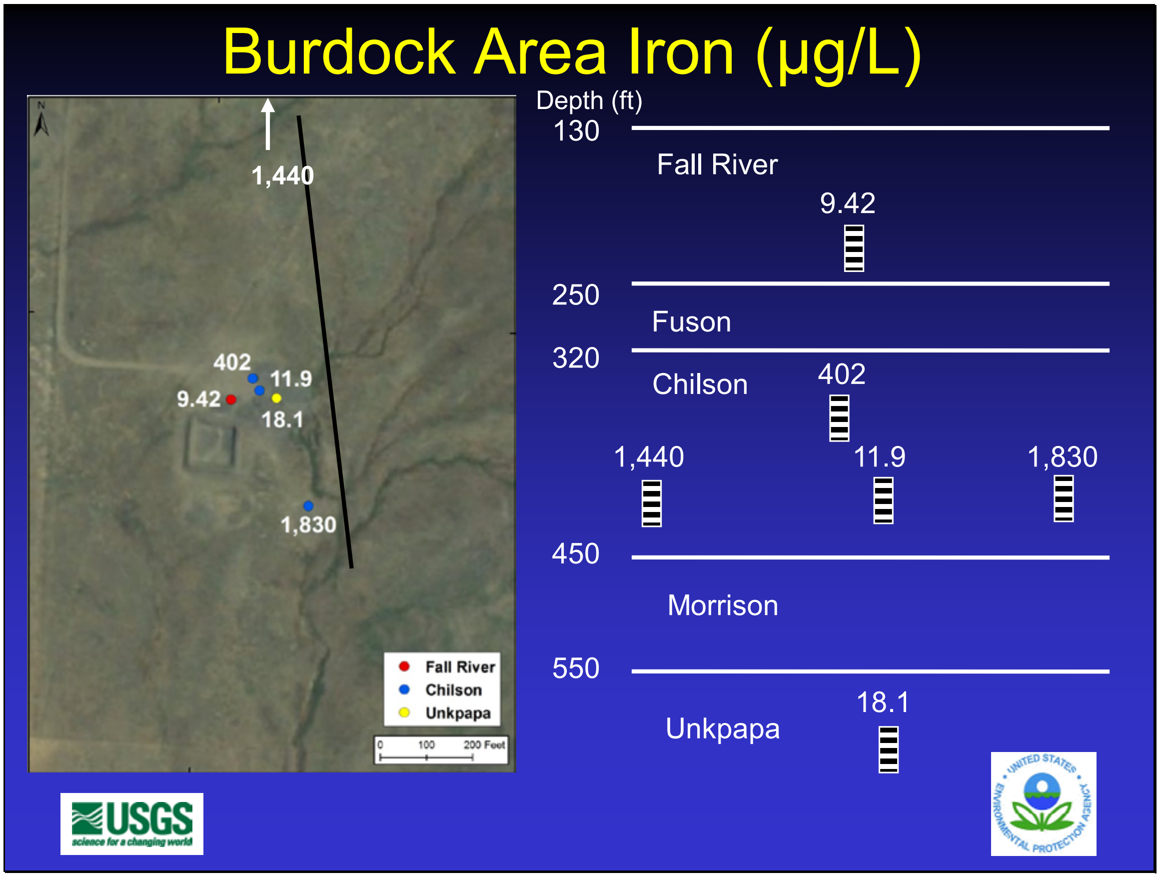
Slide 64


Dewey Area Iron (µg/L)
133
62.2
56.5
5.10
876
9.26
Fall River
Chilson
Unkpapa
0
75
150 Feet
Depth (ft)
475
Fall River
5.10
133
56.5
9.26
610
Fuson
670
62.2
Chilson
765
Morrison
860
876
Unkpapa
USGS
science for a changing world
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Slide 65



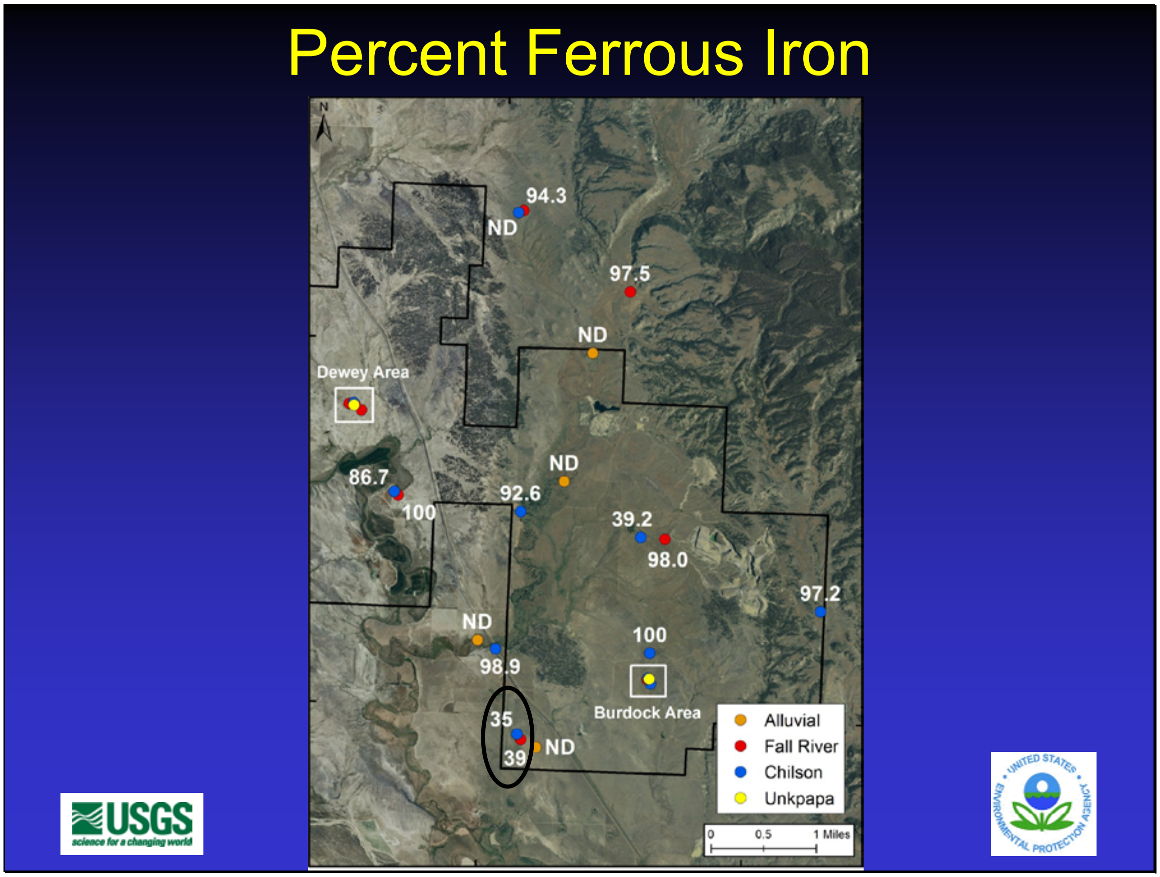
Wells 682 and 684 (14.5 and 22.1 ppb uranium and 1,440 and 1,830 ug/L iron) have some screening in the oxidized zone.
Well 680 (11.9 ug/L iron) is fully screened in a reducing zone.

Slide 66

Ferrous Iron

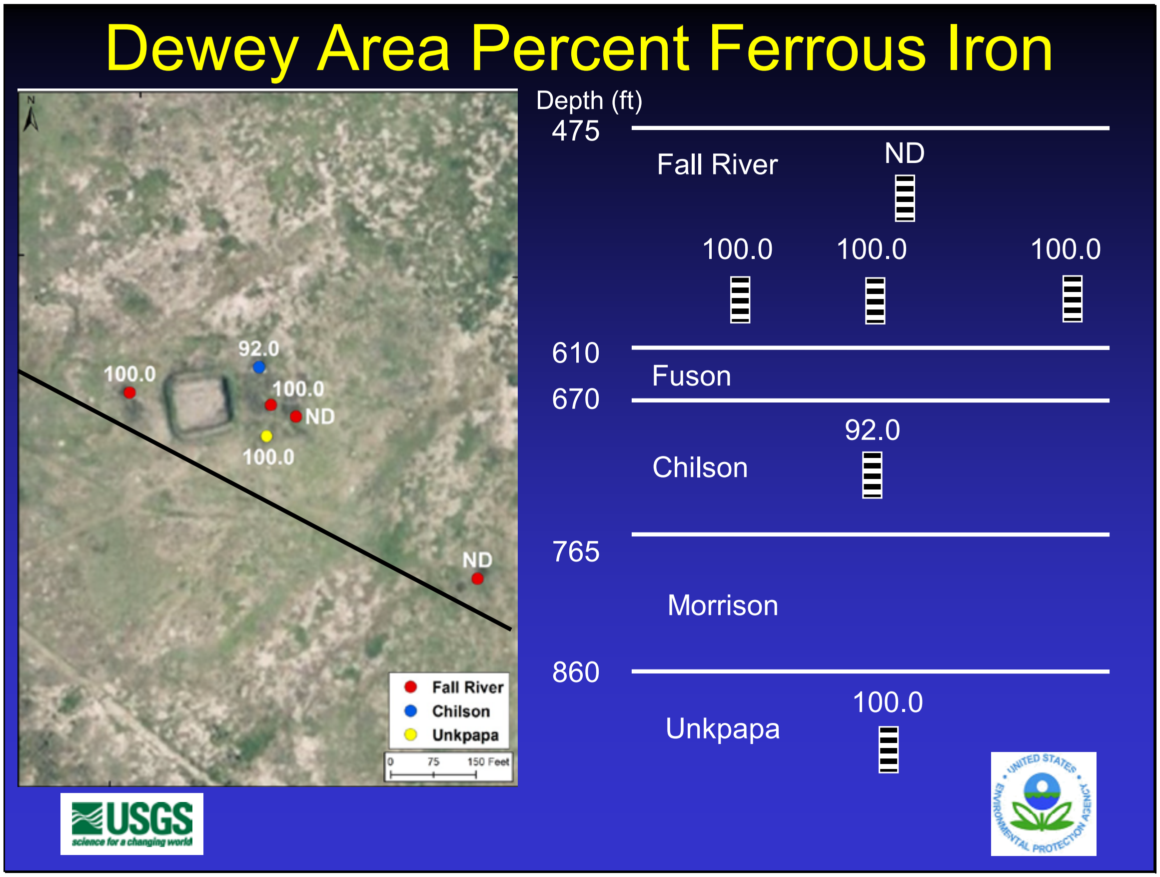
- Groundwater without dissolved oxygen would be expected to have a higher amount of ferrous iron vs. ferric iron
- Ferrous iron indicates reducing conditions, ferric iron indicates oxidizing conditions
- Groundwater with low overall iron concentrations may have inaccurate ferrous iron amounts
- Alluvial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

Slide 67



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.

Slide 68



Dewey Area Percent Ferrous Iron
100.0
92.0
100.0
ND
100.0
ND
Fall River
Chilson
Unkpapa
0 75 150 Feet
Depth (ft)
475
Fall River
ND
100.0
100.0
100.0
610
Fuson
670
92.0
Chilson
765
Morrison
860
100.0
Unkpapa
USGS
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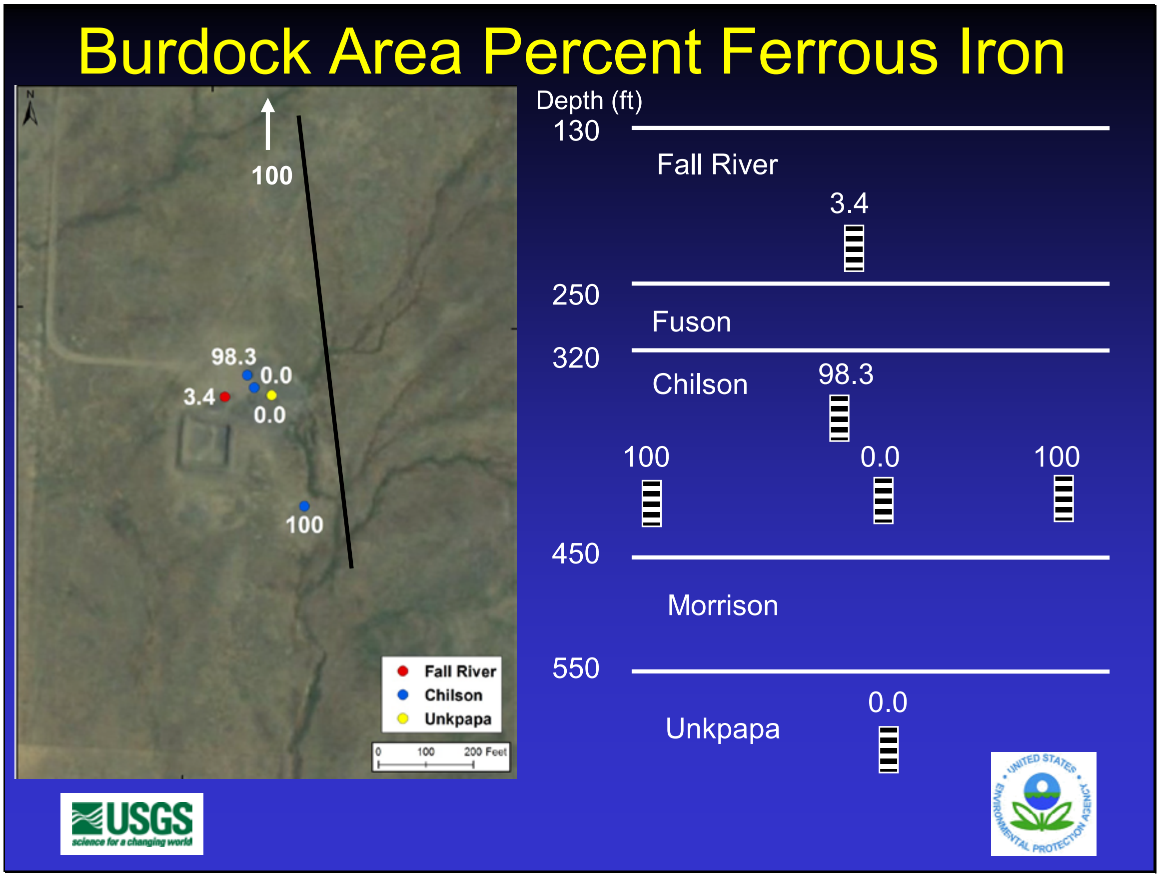
Slide 69

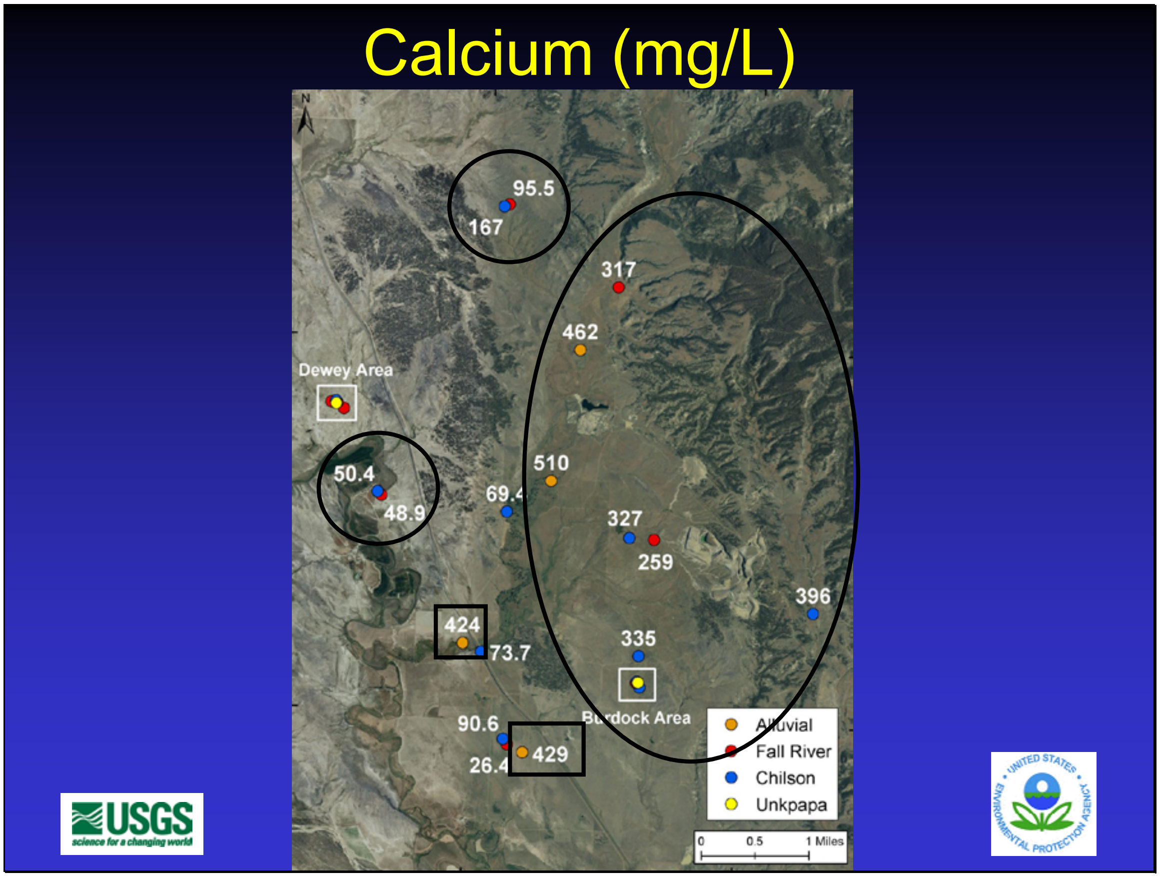


Burdock Area Percent Ferrous Iron
100
98.3
0.0
3.4
0.0
100
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
3.4
250
Fuson
320
Chilson
98.3
100
0.0
100
450
Morrison
550
Unkpapa
0.0

Slide 70

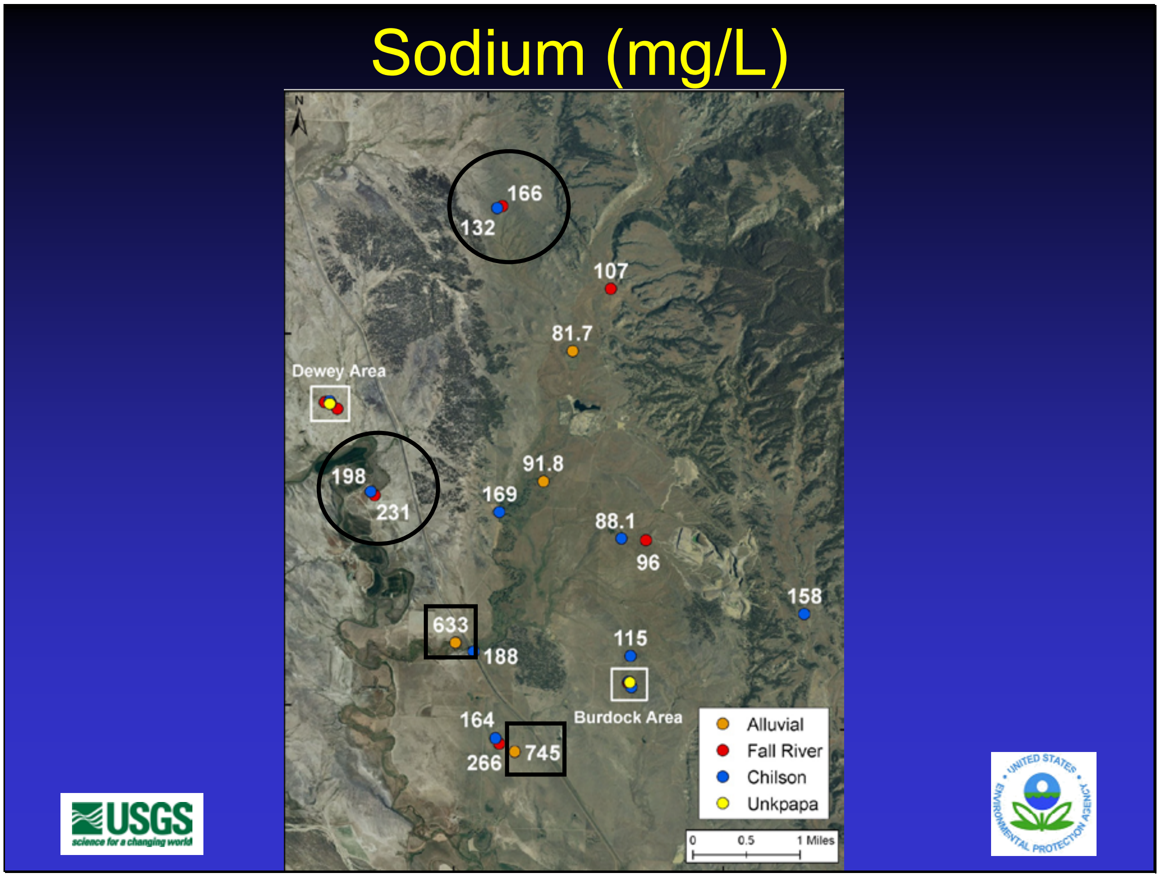
Calcium and Sodium

- 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



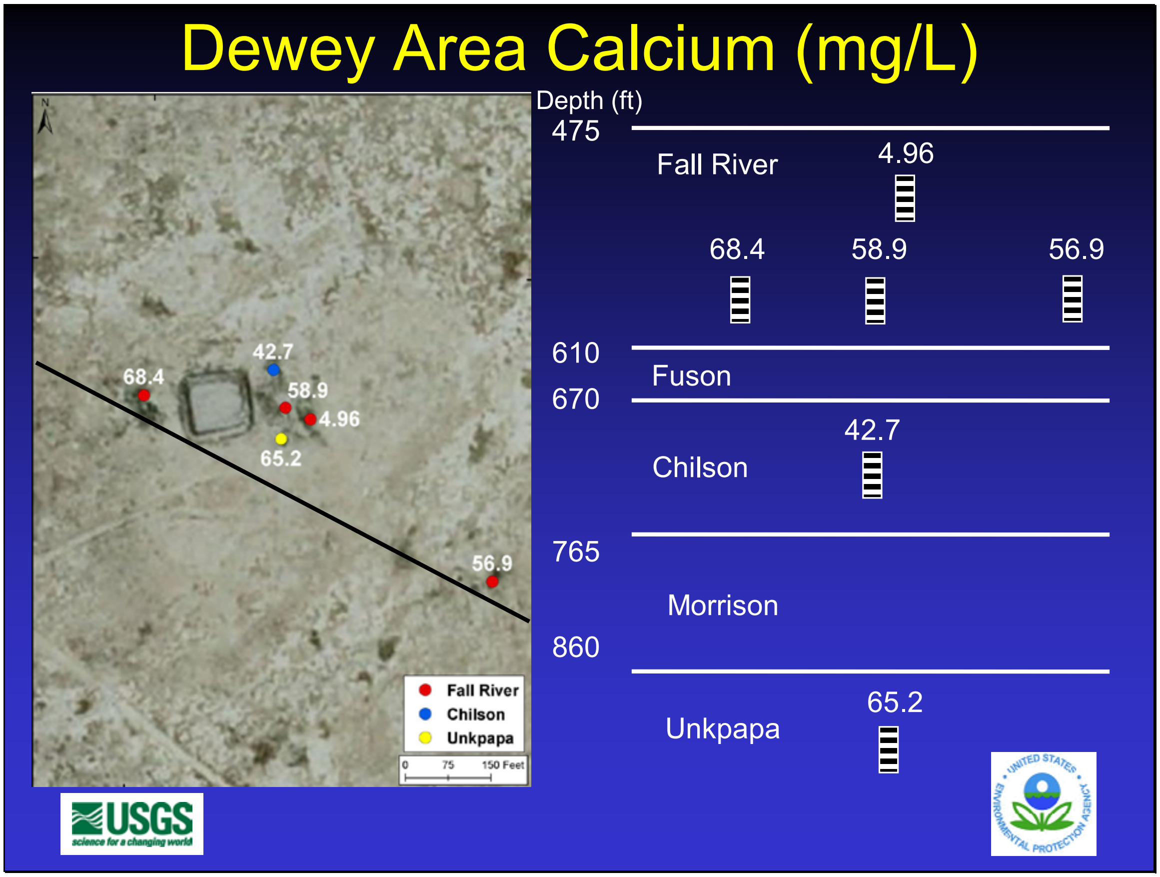
Large circle indicates high calcium values in the Burdock area.
Rectangles indicate high calcium in alluvial wells.
Circles indicate lower calcium values in the Dewey area.

Slide 72



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

Slide 73



Dewey Area Calcium (mg/L)
Depth (ft)
475
Fall River
4.96
68.4
58.9
56.9
610
Fuson
670
Chilson
42.7
765
Morrison
860
Unkpapa
65.2
42.7
68.4
58.9
4.96
65.2
56.9
Fall River
Chilson
Unkpapa
0 75 150 Feet
USGS
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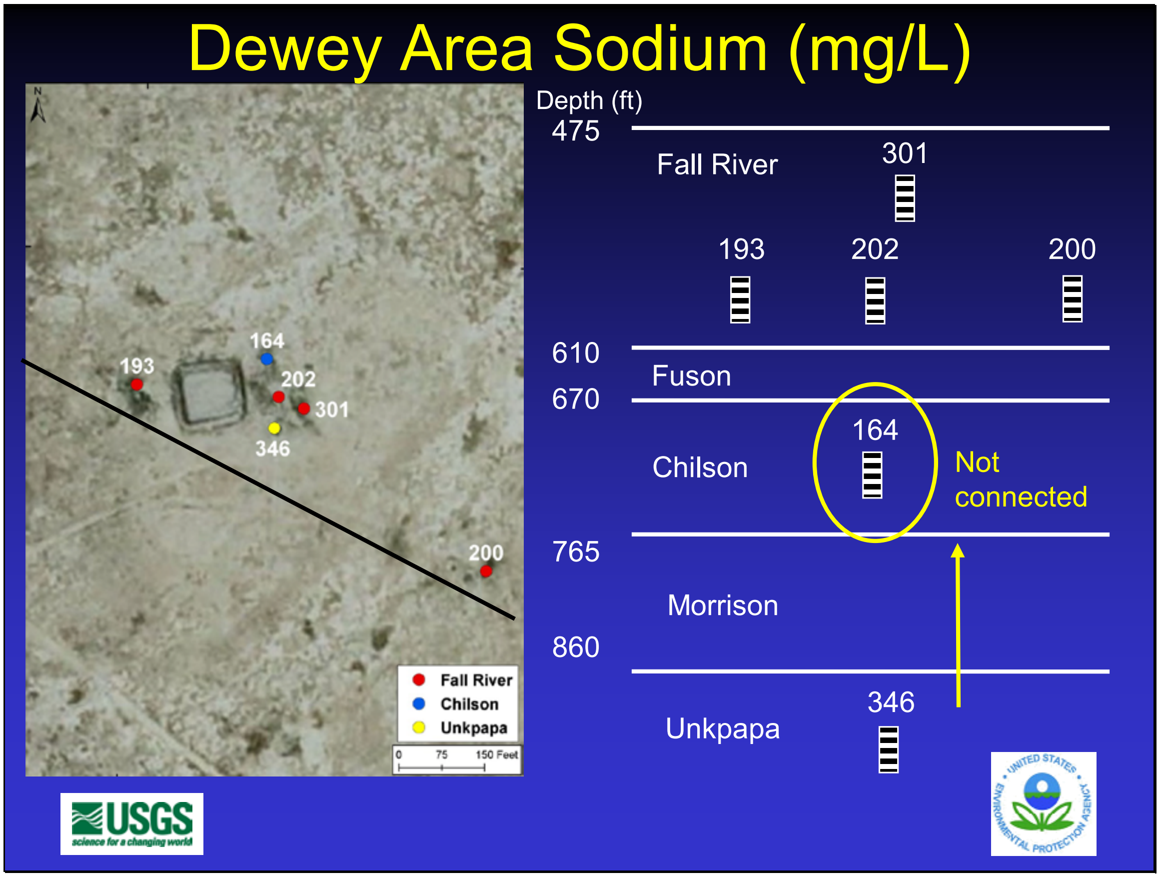
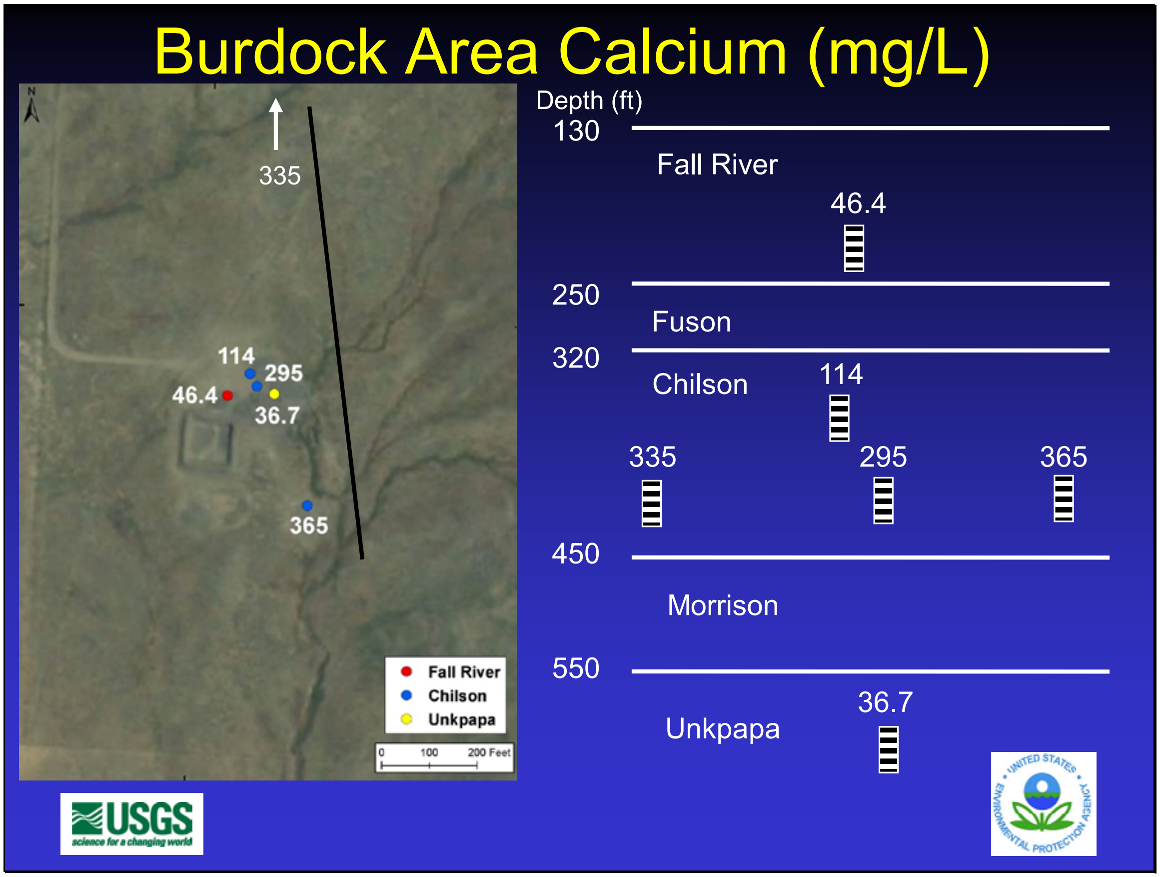
Slide 74

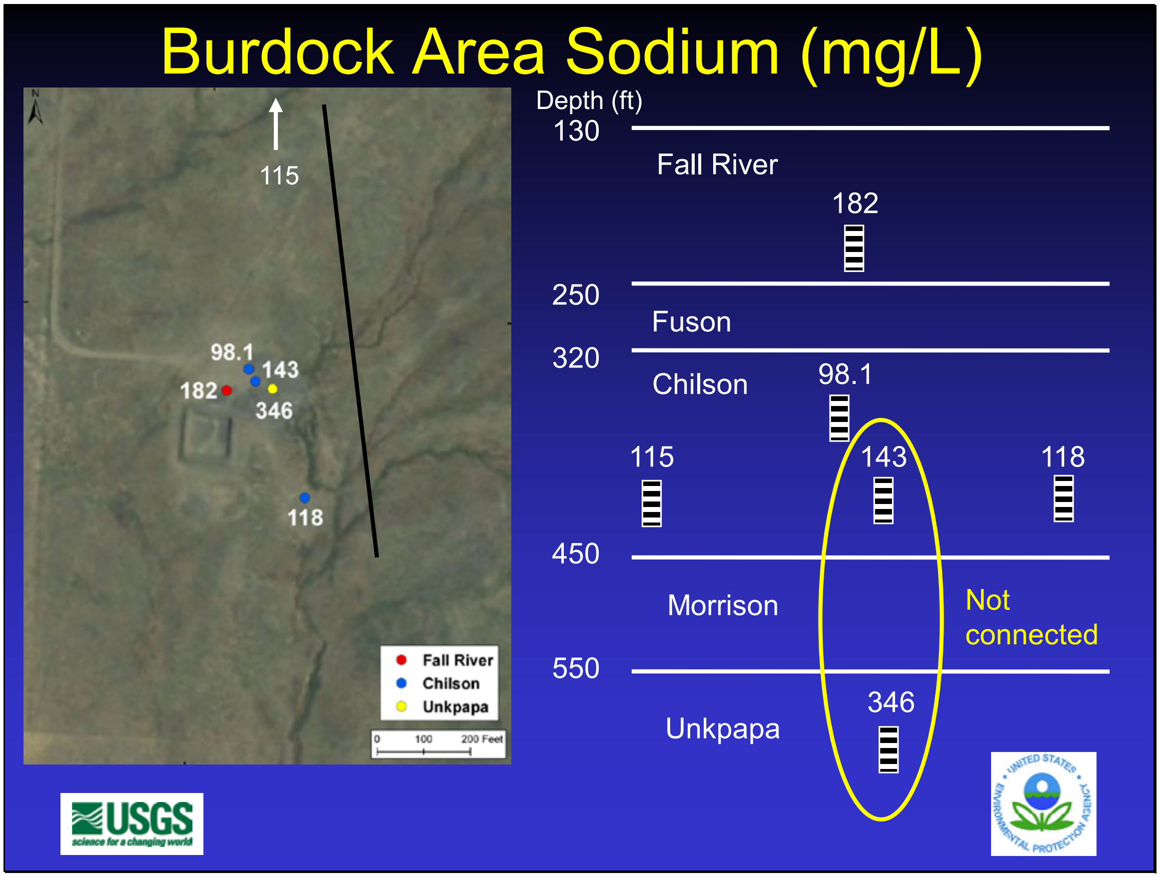


Sodium should be relatively conservative (or if anything should increase), so significant upward flow of groundwater from the Unkpapa is not indicated.

Slide 75


Burdock Area Calcium (mg/L)
335
114
295
46.4
36.7
365
Fall River
Chilson
Unkpapa
0
100
200 Feet
Depth (ft)
130
Fall River
46.4
250
Fuson
320
Chilson
114
335
295
365
450
Morrison
550
Unkpapa
36.7
USGS
science for a changing world

Slide 76



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

Slide 77

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.

Slide 78

Groundwater Geochemistry Summary and Interpretations (cont.)

- Source of groundwater recharge away from Pass Creek is unclear (dramatic ^{18}O differences)
- Major geochemistry (Ca, Na, and Sulfate) differences between Dewey and Burdock areas may be to 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)