Evaluation of Water Quality Variability for Uranium and Other Selected Parameters in Walnut Creek at the Rocky Flats Site

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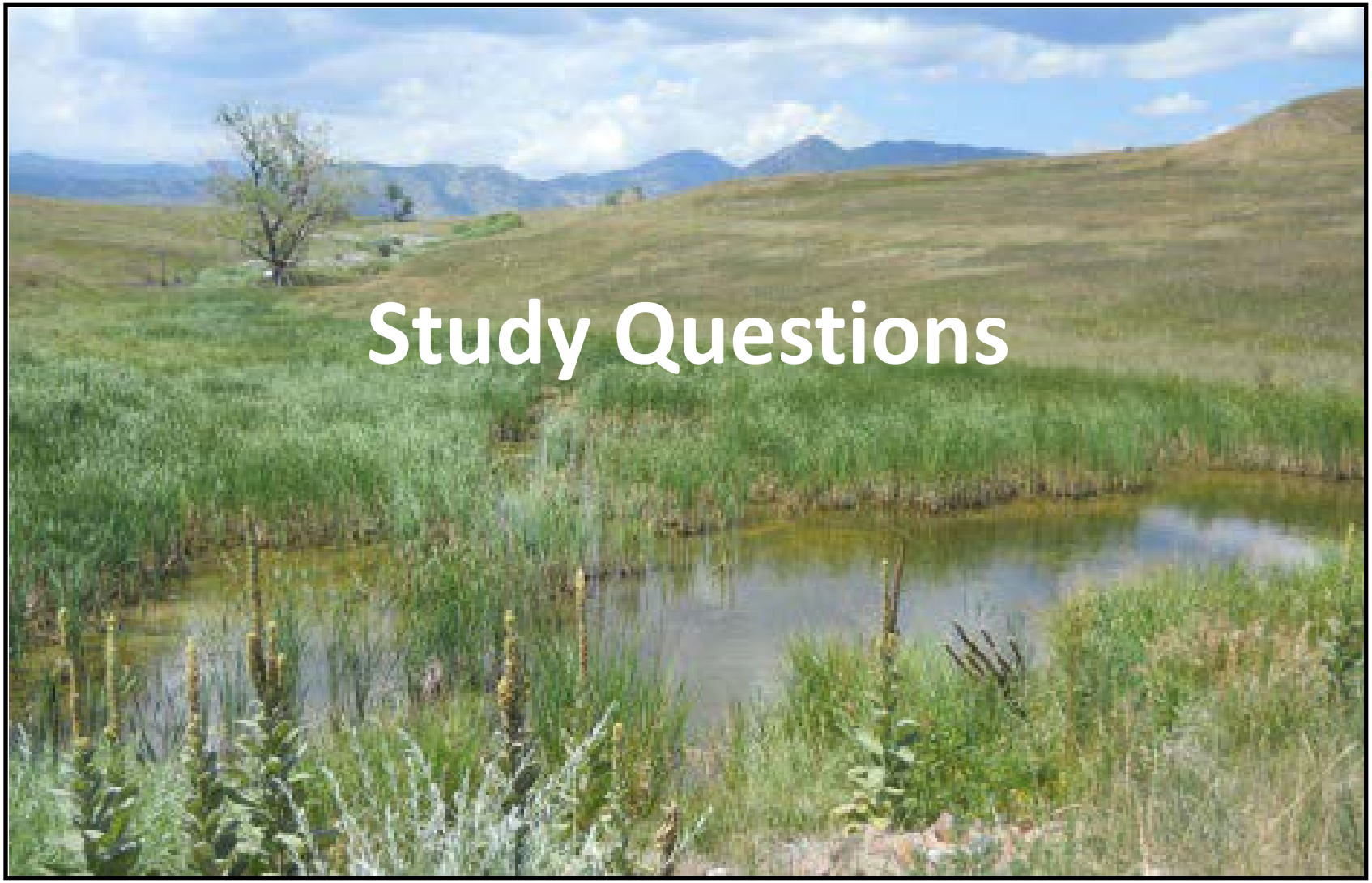

Study Questions

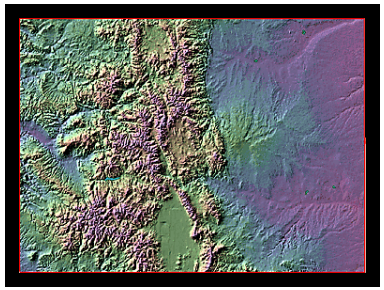
Background Information

Study Questions

Three Questions Addressed:

1) How do concentrations of natural uranium observed globally and throughout Colorado compare with the uranium concentrations observed in the Rocky Flats Site (RFS) Walnut Creek drainages?

Natural uranium



Colorado

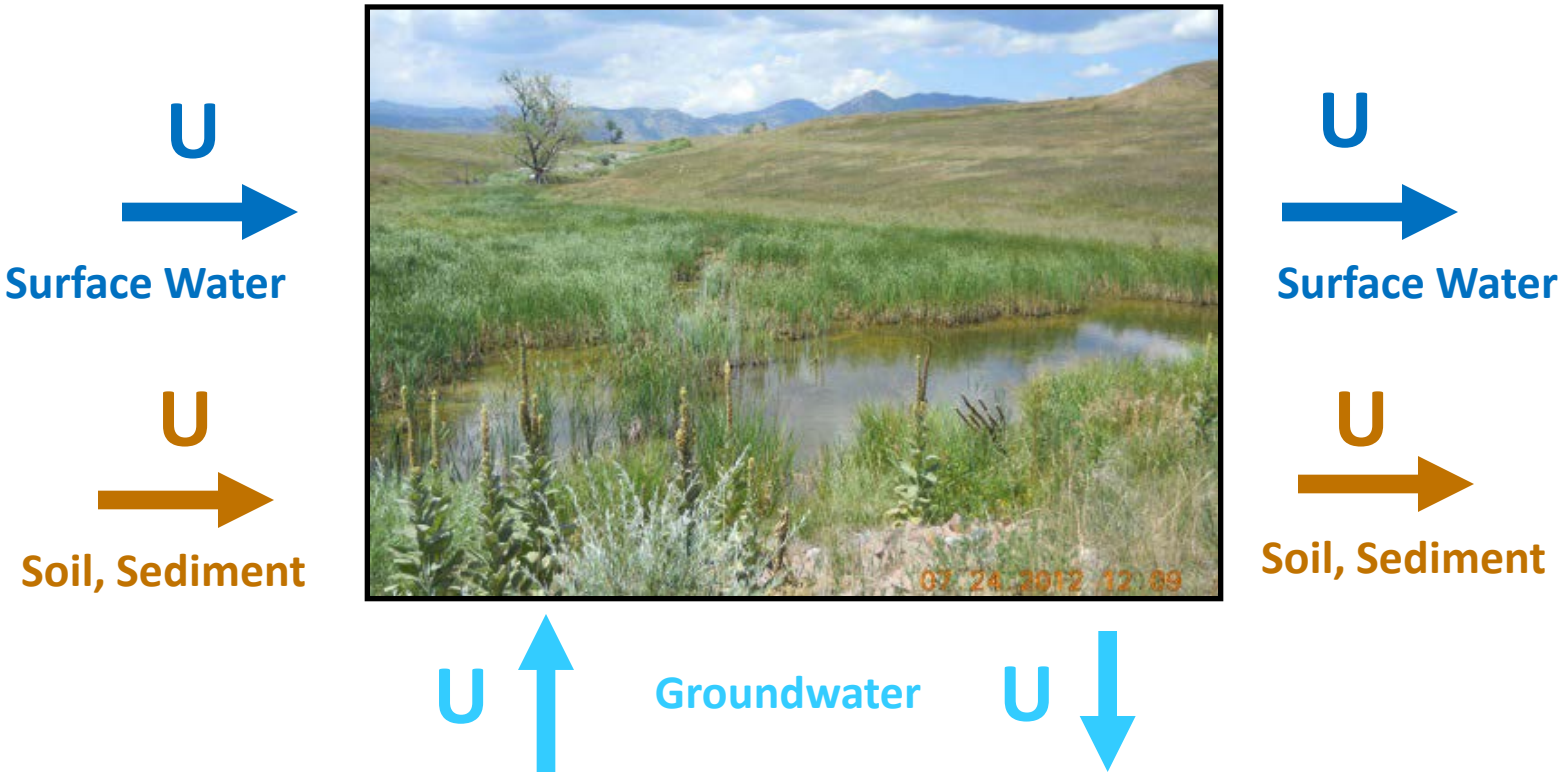
RFS – Walnut Creek

Background Information

Study Questions

Three Questions Addressed:

2) What are the primary mechanisms by which concentrations of uranium in surface water may increase and decrease?



Background Information

Study Questions

Three Questions Addressed:

3) Are previously unrecognized anthropogenic uranium sources suggested by the data?

Anthropogenic U ?

Surface Water

Soil, Sediment

Groundwater

Background Information

Background Information

Presence of Natural Uranium in the Environment – Geologic Material

- **Natural Uranium Occurrence**
  - Ubiquitous throughout world
    (About as abundant as tin or zinc)

Natural Uranium in Earth's Crust	**Concentration (mg/kg) (ppm)**
Average concentration	~ 2 - 3
Natural Uranium – By Type of Geologic Formation	
Sedimentary Formations	~ 1.3
Granitic Formations	~ 2 – 15
Phosphorus-bearing Formations	~ 20 - 120
Very low to low-grade uranium ore	~ 100 – 1000
High to very high grade uranium ore	~ 20,000 – 200,000

Sources: Langmuir, 1997; World Nuclear Association, 2015.

Background Information

Presence of Natural Uranium in the Environment - Water

Natural Uranium – By Type of Water	Concentration (µg/L) (ppb)
Sea water	~ 2 – 3.7
Streams (U.S.) – Typical	~ 0.1 – 0.7
Streams (U.S.) – Uranium mining areas (typ.)	~ 1 - 10
Streams (U.S.) – Irrigated area runoff	Up to 20 +
Groundwater (U.S.) - Uranium mining areas (typ.)	~ 1 - 120

Sources: Langmuir, 1997; Fix, USGS and AEC, 1955.

Uranium Standards in Surface Water (for Reference)	Concentration (µg/L) (ppb)
EPA Drinking Water Maximum Contaminant Level (MCL)	30 µg/L
Rocky Flats Site-Specific Standard	16.8 µg/L

Background Information

Isotopic Composition of Uranium

Magenta:
Man-Made U isotopes

Uranium Type		Main Uranium Isotopes – % by Mass				
		U-233	U-234	U-235	U-236	U-238
Natural		0.000	0.0057	0.7202	0.000	99.27
Anthropogenic	Depleted (U-235 removed)	<0.005	<0.01	0.25	<0.01	99.75
	Highly Enriched (U-235 concentrated)	0.002	1.007	95 - 97	0.4	3 - 5

Mostly U-238

Less U-235

Mostly U-235

Specific Activity (Radioactivity Per Unit of Mass)

Lowest to Highest Specific Activity

Isotope	Specific Activity (Ci/g)	Origin
U-238	3.33×10^{-7}	Original U isotope on Eart
U-235	2.14×10^{-6}	Original U isotope on Eart
U-236	6.3×10^{-5}	Neutron capture in nuclea
U-233	9.5×10^{-3}	Neutron capture in nuclea
U-234	6.25×10^{-3}	In decay chain of U-238

Depleted U has a lower % of U-235 and higher % of U-238 than natural U;

Therefore Depleted U is <u>less</u> radioactive than natural U (by mass)

Uranium from natural and anthropogenic sources has the same chemical behavior in the environment

Background Information

Uranium Standards in Surface Water

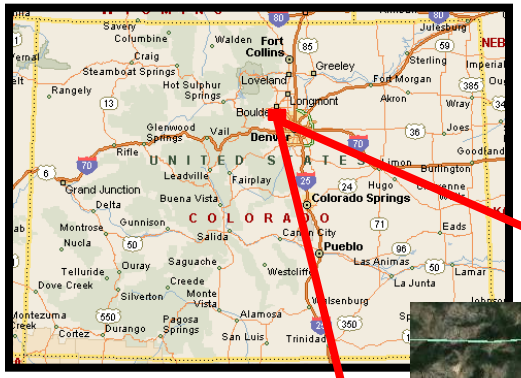
Uranium Standard	Concen. (µg/L)	Comment
Drinking Water **Maximum Contaminant Level (MCL)**	**30**	**Determined by EPA** **- Acceptable level in public water supplies** (Accounts for treatability , lab detection limits, and health effects: 1 x 10^{-4} increased cancer risk based on consumption of 2 liters of water per day for 70 years)
Colorado **Statewide Stream Standard** **(for Domestic Water Supply)[1,2]** [1]Per CDPHE CQCC Reg. 31, Domestic Water Supply waters are suitable or intended to become suitable for potable water supplies after receiving standard treatment; [2]Uranium standards for other usage classifications also exist (Aquatic Life acute and chronic standards); values for both standards vary as a function of water hardness.	**16.8 - 30**	**Hyphenated Standard** **- 16.8 µg/L is health-based value[3]** **- 30 µg/L is MCL** **(see above)** [3]Calculated per WQCC Policy 96-2, based on chemical toxicity and consumption of 2 liters of water per day
Rocky Flats Site **Site-Specific Stream Standard**	**16.8**	**Per RFLMA** **Measured at POCs** - **30-Day Avg.** (Reportable Condition) - **12-Month Rolling Avg.** (Reportable Condition + Compliance Evaluation)

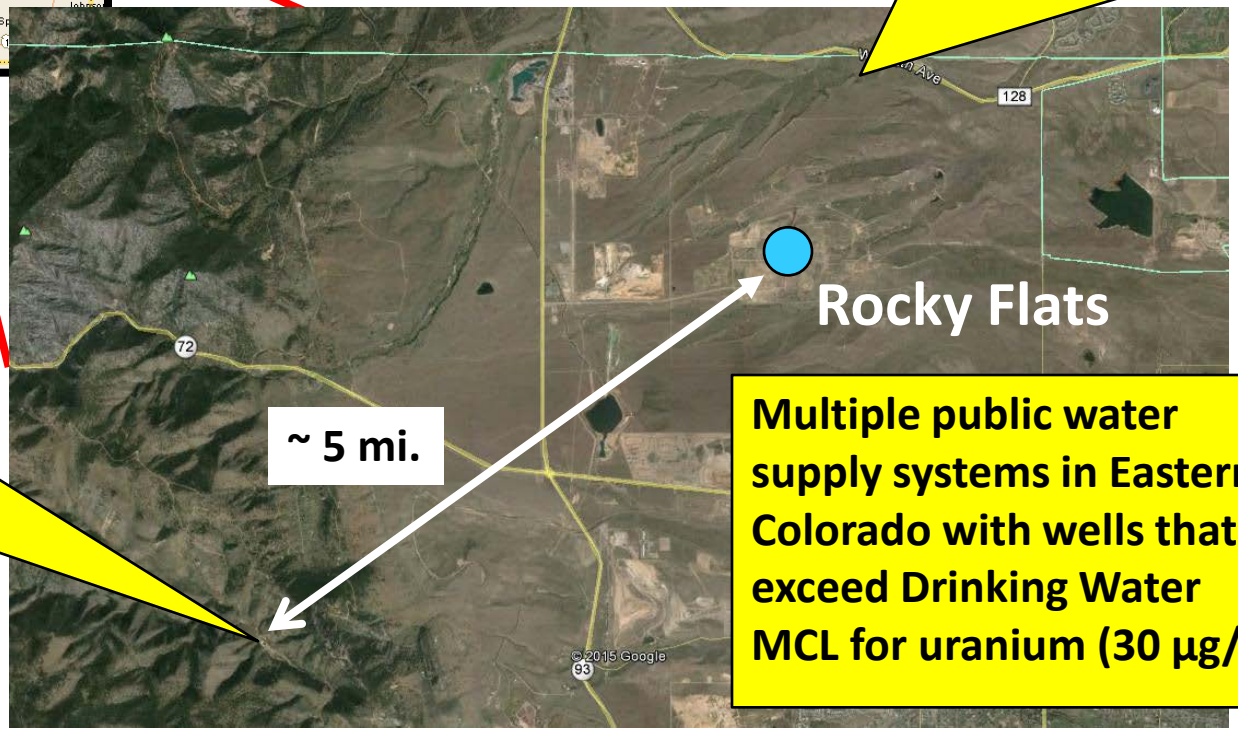
Background Information

Colorado Front Range - Above Average Natural Background Uranium

Rock Creek Surface Water Sampling Location SW004
Uranium up to > 20 µg/L (Background Geochem. Study)
(Total U, March 1989.; Source: EG&G, 1990)

Rock Creek is a reasonable analog for natural background uranium in groundwater at RFS
(Source: USGS, 2000)





Schwartzwalder Uranium Mine

Largest vein-type uranium deposit in United States

Multiple public water supply systems in Eastern Colorado with wells that exceed Drinking Water MCL for uranium (30 µg/L)

Background Information

Chemical Processes that Affect the Mobility of Uranium

- Precipitation Reactions (formulation of solid U species)
- Dissolution Reactions (formulation of soluble U species)
  - Influenced By:

- Redox Potential
  - Dissolved Oxygen
  - Nitrate

} Change with environmental conditions at RFS

- Sorption

} Influenced by Dissolved Oxygen and Nitrate

- pH
- Complexation Reactions

} Relatively constant at RFS

These processes involve interactions between surface water, groundwater, soil and sediments

Background Information

Chemical Processes that Affect the Mobility of Uranium

Oxidation State Affects Environmental Behavior

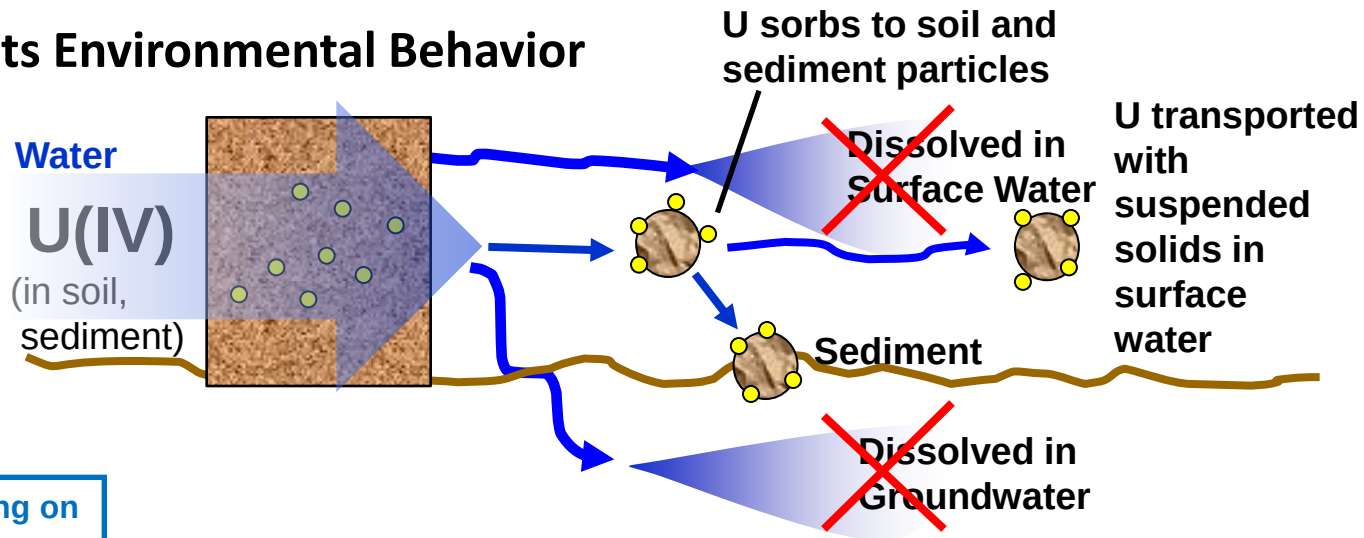
U^{4+}

Lower Oxidation State

Essentially Insoluble

Present in reducing conditions

(e.g., anaerobic sediment, wetlands, etc.)



Reversible depending on presence of oxidizing agents

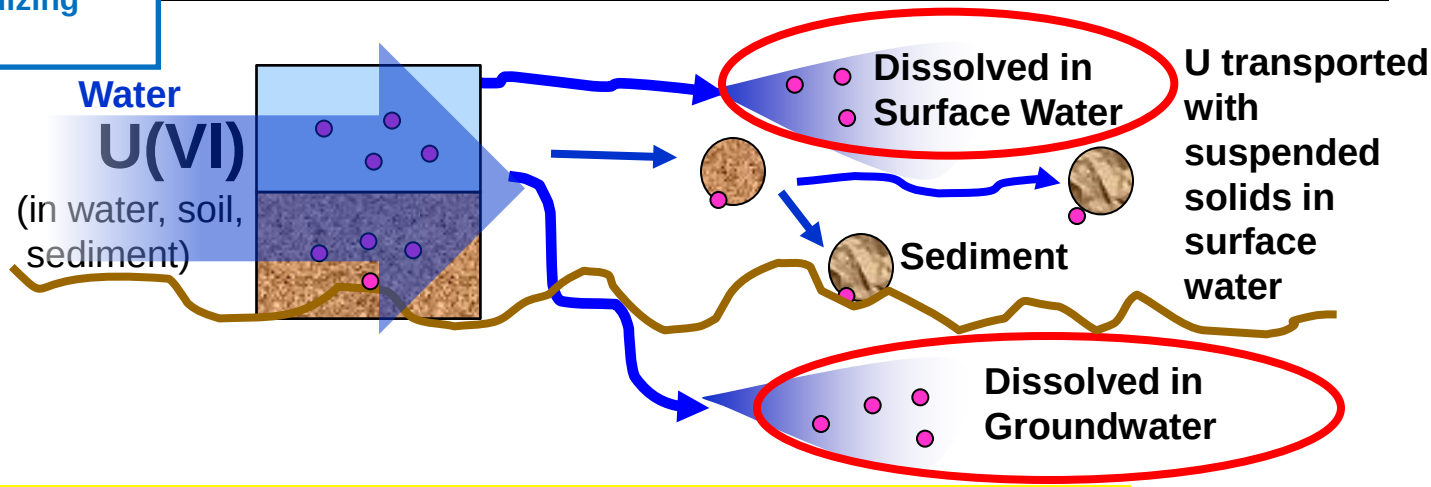
Present in oxidizing conditions

(Oxidizing agents: O_2, NO_3, Mn, Fe, etc.)

U^{6+}

Higher Oxidation State

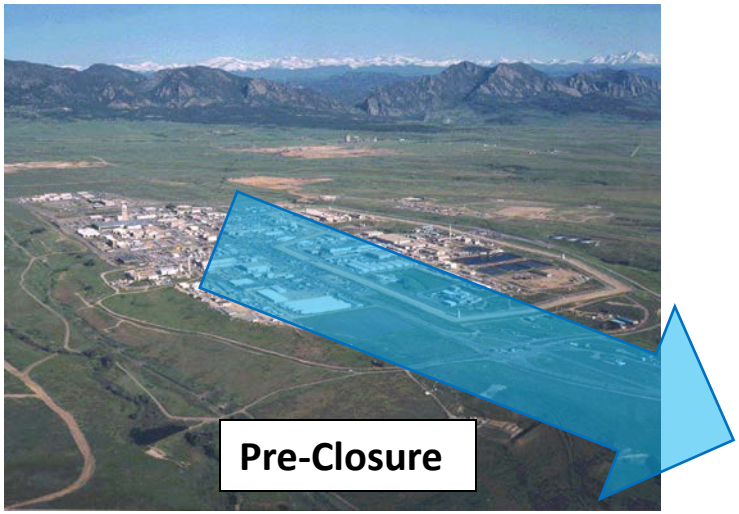
More Soluble



Whether uranium is from natural or anthropogenic sources, it has the same chemical behavior in the environment

Background Information

RFS – Changes That Affected Uranium Concentrations in Surface Water



"Additional" Surface Water
- Runoff from impervious surfaces
- Imported water
  (Discharged from WWTP as treated effluent)

Result: <u>Lower</u> uranium concentrations in surface water

"Additional" Surface Water
- None

Result: <u>Higher</u> uranium concentrations in surface water

Background Information

Data Compiled and Analyzed

Question 1:

(Compare concentrations of natural uranium globally and in Colorado with the uranium concentrations observed at RFS)

- Literature review
- Review of CDPHE records (for water quality in public water systems)
- DOE historic reports

Question 2:

(What are the primary mechanisms by which concentrations of uranium in surface water may increase and decrease?)

- Surface water (uranium and nitrate), 1997 – 2014, focus on 2010 - 2013
- Surface water, sediment (multiple additional parameters), 2012 - 2014

Question 3:

(Are previously unrecognized anthropogenic uranium sources suggested by the data?**)**

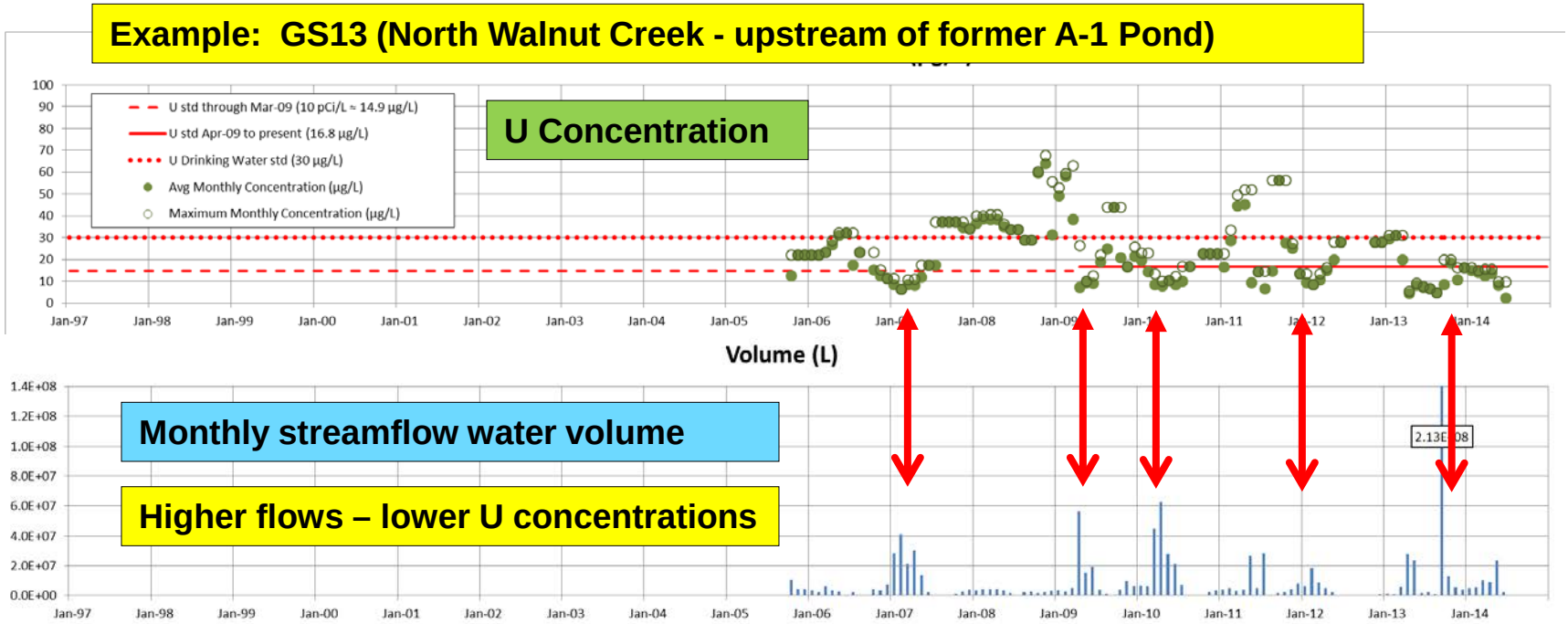
- Surface water and groundwater, U isotopic analyses (TIMS and ICP/MS)
- LANL and LBNL
- 2002 - 2014

Main Observations

Main Observations

Uranium Concentrations in Surface Water

- **Uranium concentrations in surface water are strongly influenced by groundwater contribution to stream channels**
  - **Groundwater from Upper Hydrostratigraphic Unit (UHSU) discharges to surface water**
  - **When stream flows are high, uranium concentrations are lower**
    (i.e., when groundwater discharges are a smaller proportion of stream flow)
  - **When stream flows are low, uranium concentrations are higher**
    (i.e., when groundwater discharges are a larger proportion of stream flow)

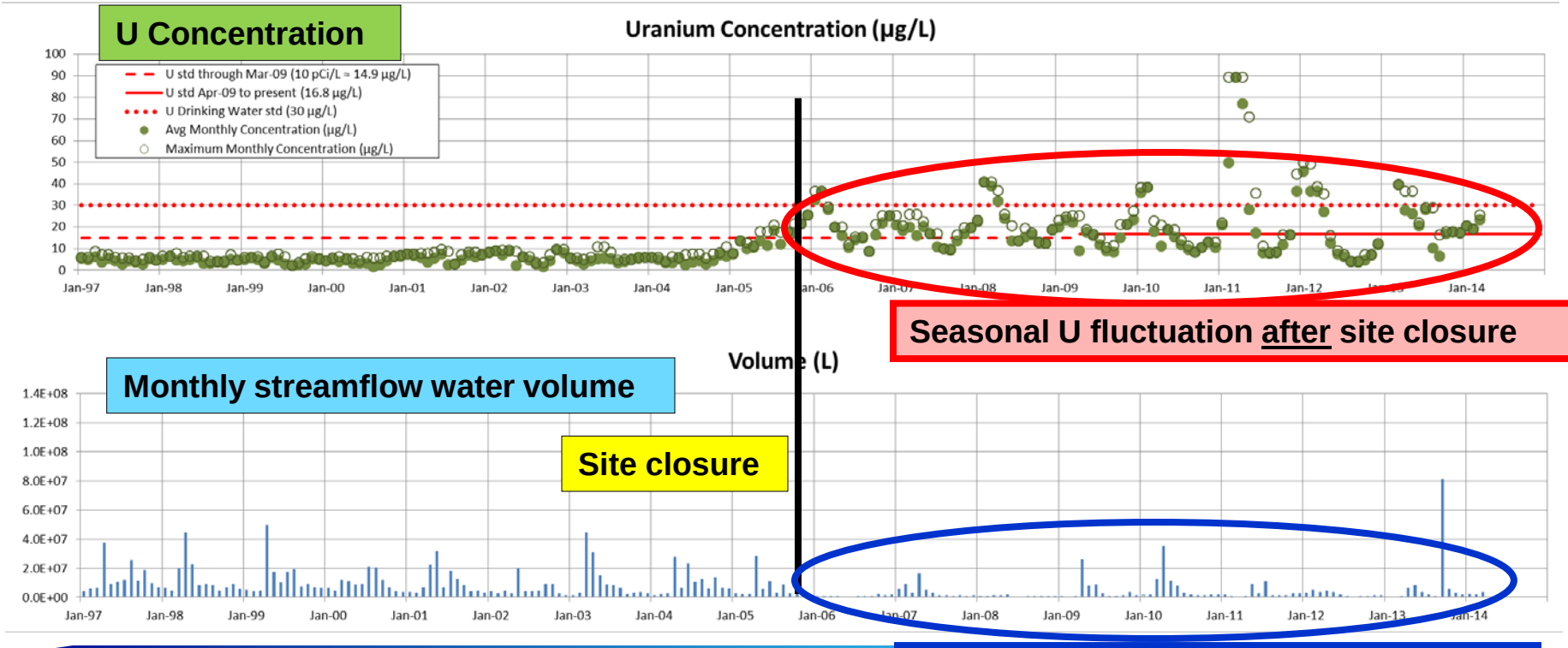


Main Observations

Uranium Concentrations in Surface Water

- **Seasonal uranium increases are more pronounced in post-closure**
  - Post-closure conditions: Less impervious area
    - Less rainfall/snowmelt goes to surface runoff

Example: GS10 (South Walnut Creek - upstream of former B-1 Pond)



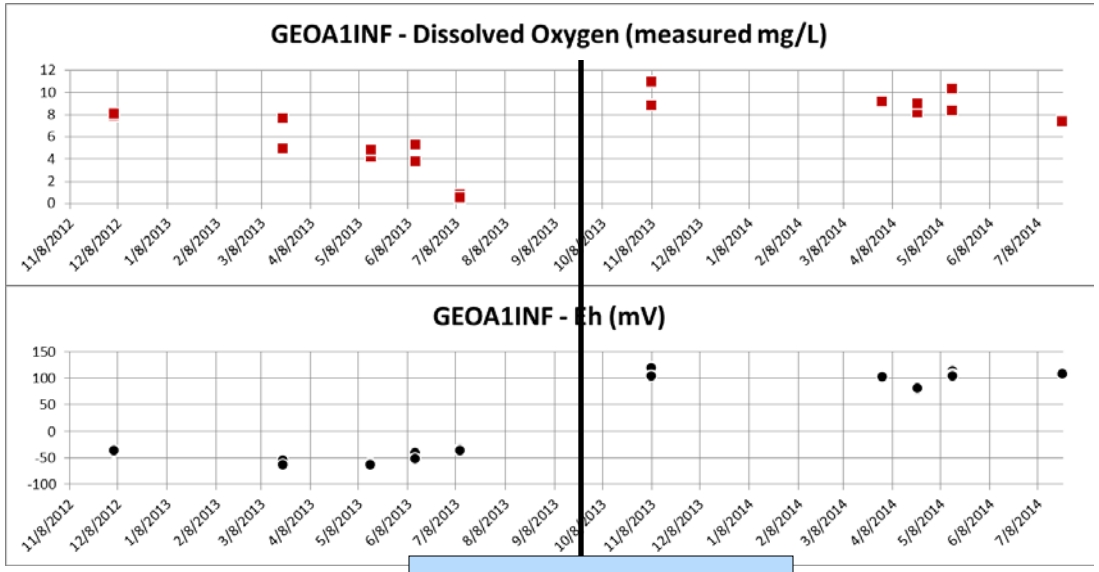
Main Observations

Effect of Large Storms

- **September 2013 Storm**
  - 6.5 inches of rainfall over approximately 7 days
    - 100-year, 7-day storm per NOAA Atlas 14, Volume 8
    - Largest 7-day precipitation on record at site
  - Slow movement of groundwater caused:
    - Prolonged increase in groundwater discharge to surface water
    - Prolonged increase in dissolved oxygen/ in surface water
    - Prolonged change in redox conditions

Example: GEOA1INF

(North Walnut Creek - upstream of former A-1 Pond)



Dissolved Oxygen

Makes groundwater oxidizing

Redox Potential

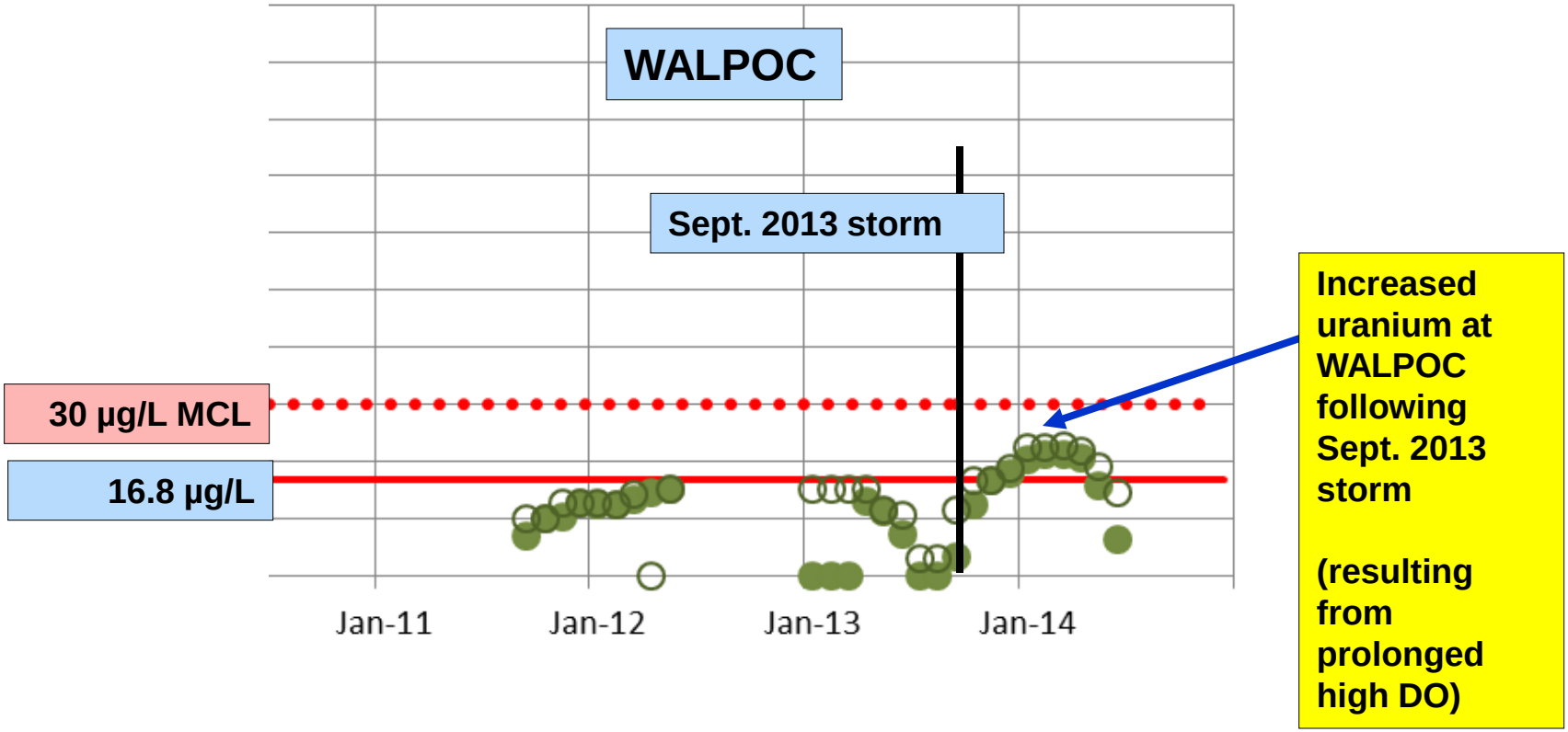
Oxidizing conditions: U(IV) to(U(VI) (More soluble)

Sept. 2013 storm

Main Observations

Effect of Large Storms (continued)

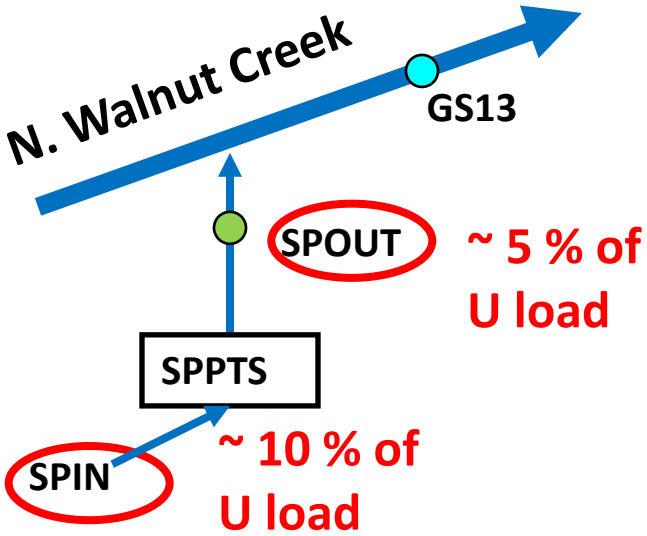
- September 2013 storm caused prolonged increase in uranium concentrations in surface water
  - Upstream locations
  - WALPOC

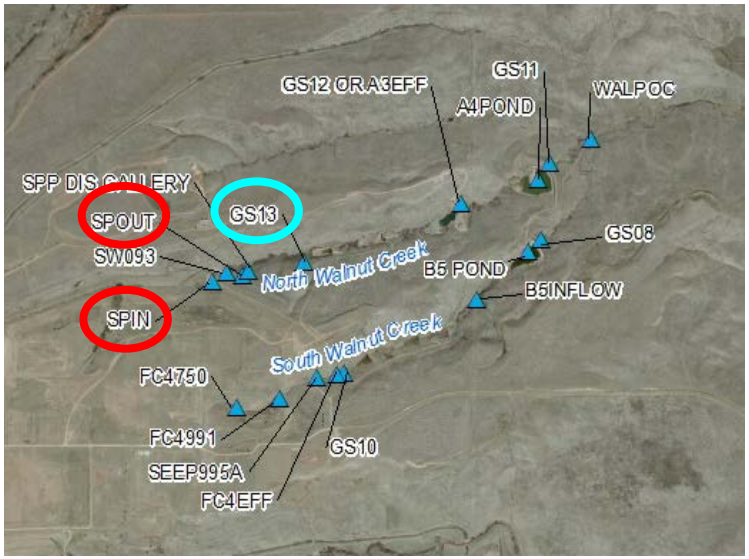


Main Observations

Solar Ponds Plume Treatment System (SPPTS)

- **SPPTS**
  - SPPTS treats the Solar Ponds Plume, which discharges to N. Walnut Creek
  - Uranium input to the SPPTS (at SPIN) is approx. 10% of U load in N. Walnut Ck.
  - Uranium discharge from SPPTS (at SPOUT) is approx. 5% of U load in N. Walnut Ck.





The SPPTS is not a major factor in terms of uranium loads in North Walnut Creek

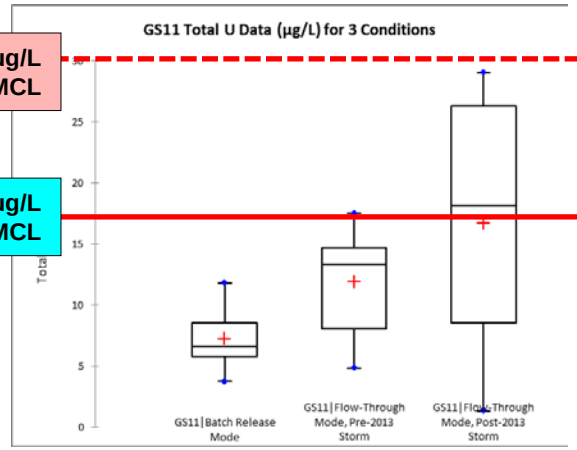
Main Observations

Effect of Large Storms: Pond A-4, Pond B-5 and WALPOC - Uranium

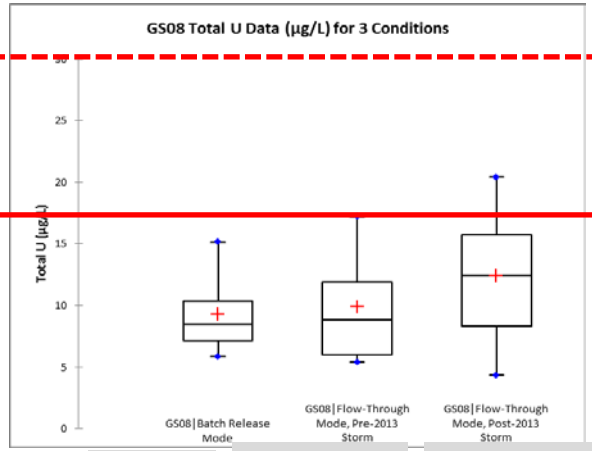
GS11 (Pond A-4 Outlet) | **GS08 (Pond B-5 Outlet)** | **WALPOC**

30 µg/L MCL

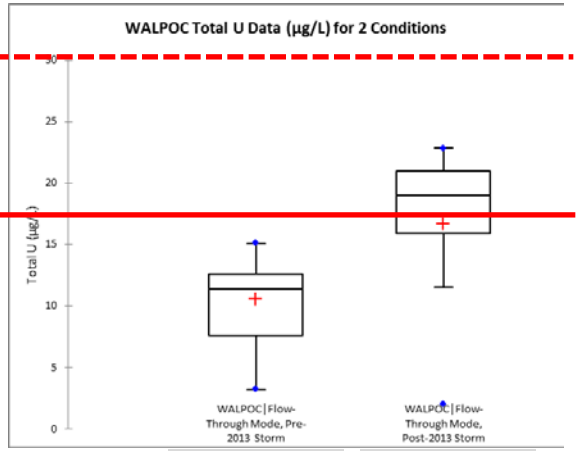
16.8 µg/L MCL



Batch | Flow-Thru Pre-2013 Storm | Flow-Thru Post-2013 Storm



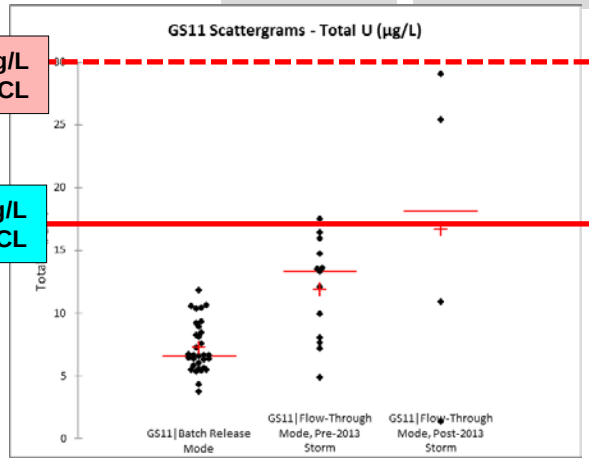
Batch | Flow-Thru Pre-2013 Storm | Flow-Thru Post-2013 Storm

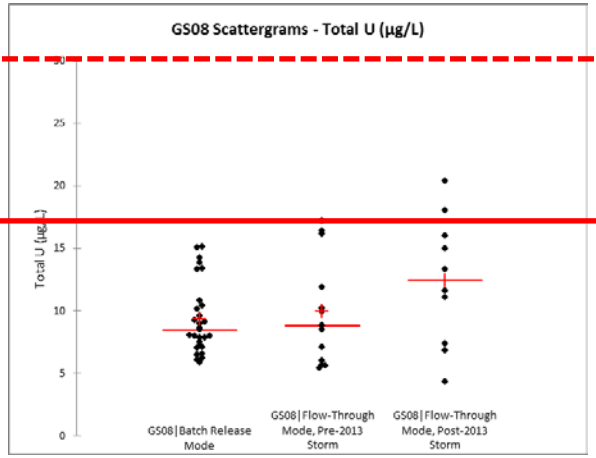


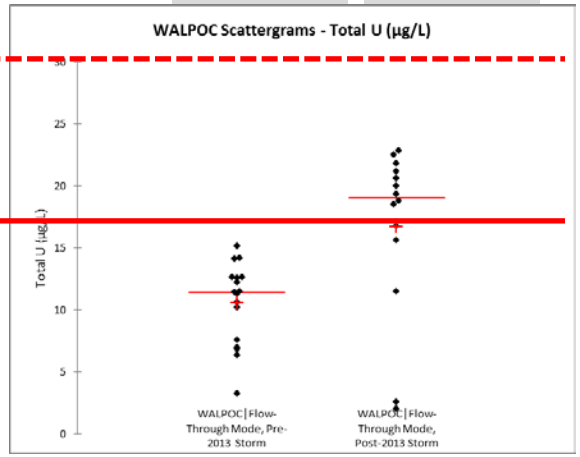
Flow-Thru Pre-2013 Storm | Flow-Thru Post-2013 Storm

30 µg/L MCL

16.8 µg/L MCL







Main Observations

Fraction of Natural Versus Anthropogenic Uranium

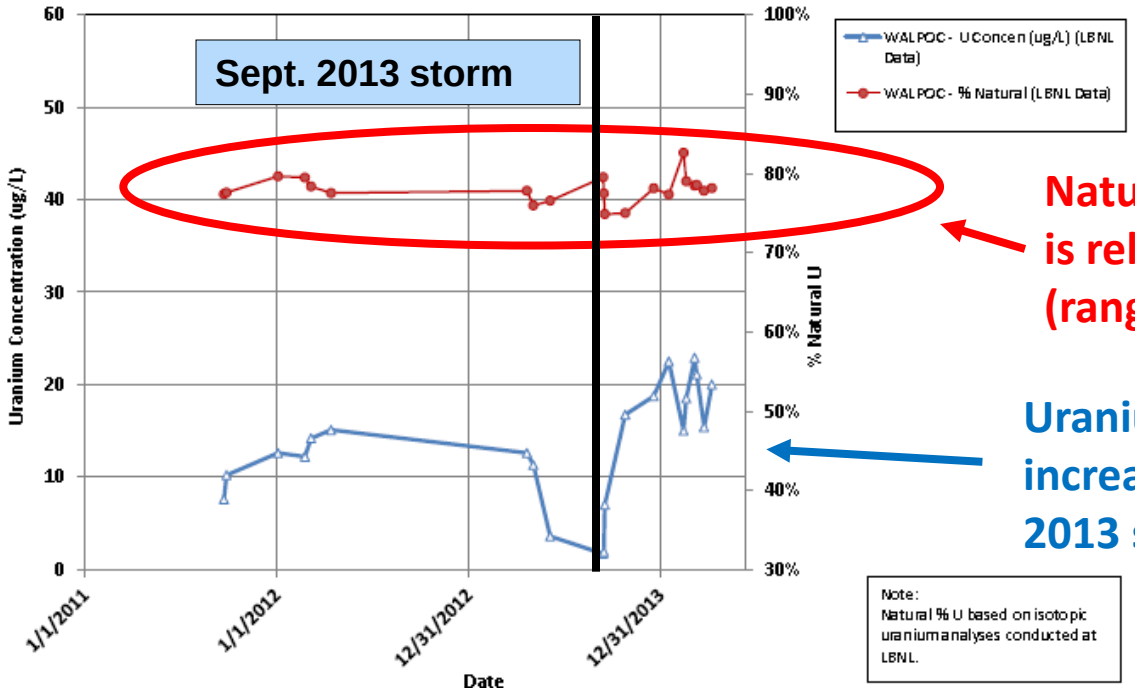
Drainage	Location	Natural Uranium Percentage		
		No. of samples (n)	(Min/Max)	Average
North Walnut Creek	GS13	5	(71.3 %/ 74.8 %)	72.6 %
	SPIN (SPPTS Inflow)	3	(47.8 %/62.0 %)	57.2 %
	SPOUT (SPPTS Outflow)	2	(57.7 %/65.1 %)	61.4 %
South Walnut Creek	GS10	17	(43.3 %/77.8 %)	65.9 %
Walnut Creek	WALPOC	21	(74.9 %/82.6 %)	78.0 %

In water collected from the Solar Ponds Plume Area, on average, over ½ the uranium has natural isotopic composition.

At WALPOC, where surface water flows off DOE site, approximately ¾ of the uranium has natural isotopic composition.

Main Observations

WALPOC - Natural Versus Anthropogenic Uranium



Natural fraction of uranium is relatively constant (range 75% – 83 %)

Uranium concentration varies, increased following September 2013 storm.

- **The natural uranium component is dominant, regardless of concentration**

- **No new anthropogenic sources of uranium indicated at WALPOC (or at other locations)**

Summary of Key Points

Summary of Key Points

- Uranium concentrations observed in surface water at RFS are expected, based on data for natural uranium at other Front Range locations, such as Rock Creek.

- The site-specific uranium stream standard at RFS (16.8 µg/L) is the low end of the range for the statewide stream standard for domestic water supplies (16.8 µg/L – 30 µg/L).

- The large storm in September 2013 had a long-term effect:
  - Prolonged positive redox potential (oxidized U(IV) to U(VI))
    - Increases mobility of uranium
  - Prolonged increased groundwater discharge to surface water
  - Prolonged increased uranium concentrations in surface water

- Pond A-4 decreases uranium concentrations more than Pond B-5.

Summary of Key Points (continued)

- The Solar Ponds Plume Treatment System (SPPTS) is not a major factor in terms of uranium loads in North Walnut Creek.

- The natural uranium component is dominant. At WALPOC, the natural fraction of uranium is consistently 75 to 83 percent, regardless of the uranium concentration.

- No new anthropogenic sources of uranium are indicated at WALPOC or other locations.

Questions/Discussion