New Mexico Environment Department

Presentation to Los Alamos County
Community Engagement

Biogeochemical Remediation of the Chromium Plume in the Regional Aquifer, Los Alamos, New Mexico
Ground Water Quality Bureau
April 6, 2022

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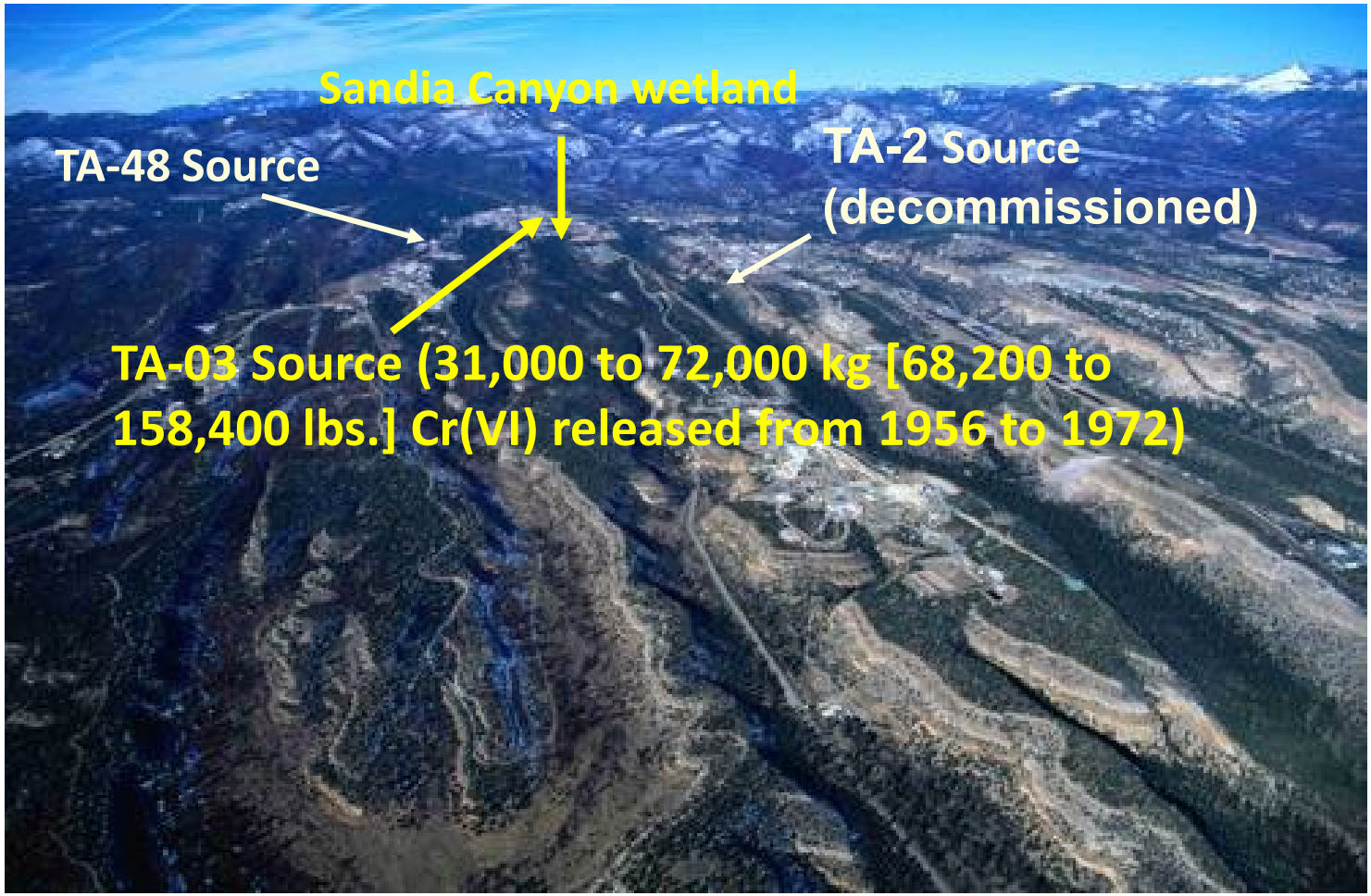
Biogeochemical Remediation of the Chromium Plume in the Regional Aquifer, Los Alamos, New Mexico

Topics of Interest

- Source(s) of Chromium
- Chromium Distributions in the Regional Aquifer
- Remediation of Chromate at Wells R-28 and R-42 and Regional Aquifer System Response.
  - sodium dithionite/sodium sulfite injection at well R-42
  - molasses injection at well R-28
  - CrEX-3
  - pump and treat
- Summary
- Path Forward

Photograph of the Jemez Mountains and Pajarito Plateau (view to the west with past industrial sources of chromium(VI) discharges)



Location Map of LANL Technical Area-03 Power Plant and Chromium Plume in the Regional Aquifer

Potassium dichromate used to control corrosion in power plant cooling towers.

158,400 lbs. released to Sandia Canyon between 1956-1972 as potassium dichromate.

Migration from perched aquifer(s) to regional aquifer formed multiple sources.

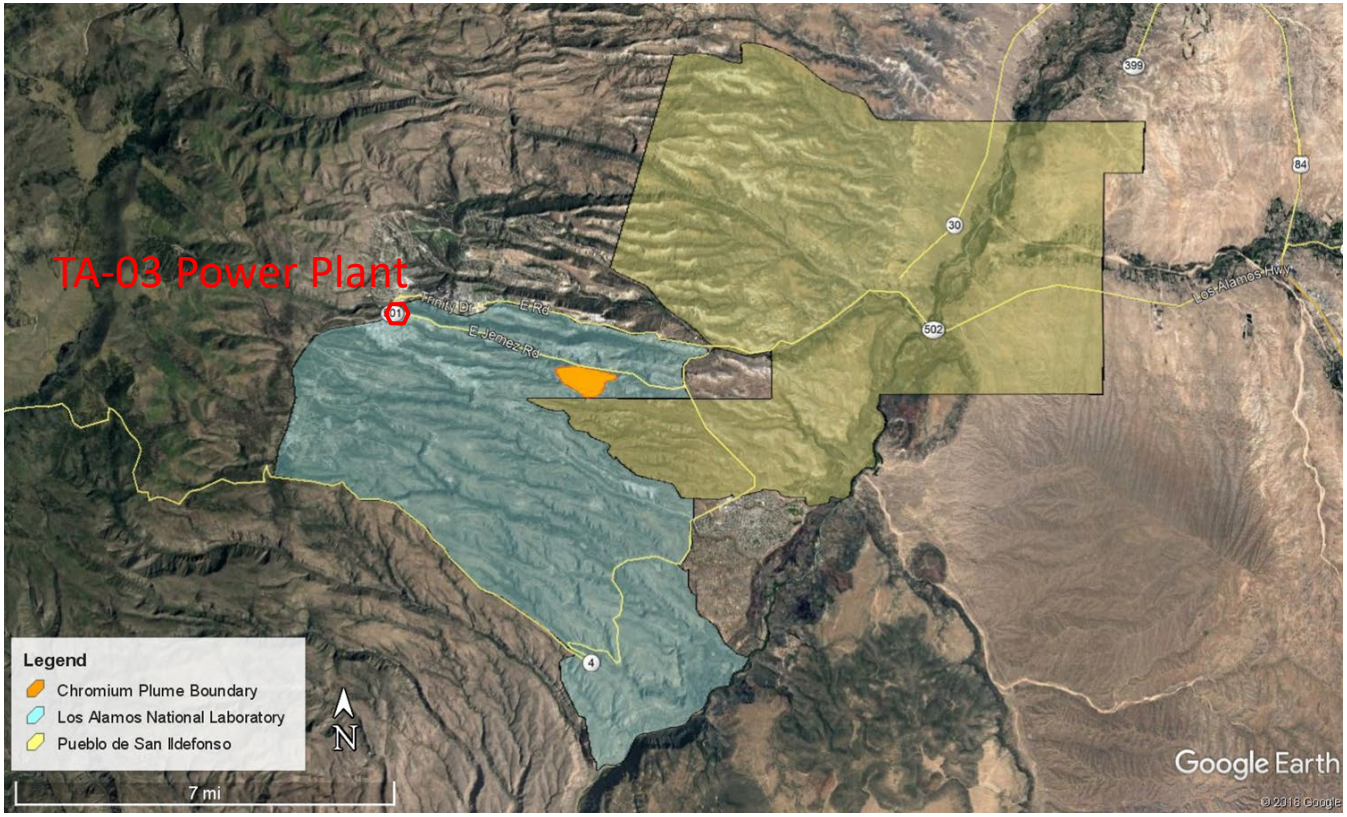
Discovered in regional aquifer in December 2005.

NMED regulates total dissolved chromium in groundwater at 50 parts per billion (ppb).

Plume is 1 mile long / half mile wide. Thickness is uncertain.

Nature & Extent remains uncertain – in Campaign Approach along with Interim Measures.

Interim Measures - mid 2018 along Pueblo de San Ildefonso boundary.



Units of Measurement

- Parts per million (ppm), 1 ppm is analogous to one second in 0.0317 years or 11.57 days.
- Parts per million is equivalent to milligrams/liter (mg/L) in most waters, excluding seawater and brines.
- Parts per billion (ppb), 1 ppb is analogous to one second in 31.69 years.
- Parts per billion is equivalent to micrograms/liter (µg/L) in most waters, excluding seawater and brines.
- Milligrams/kilogram (mg/kg) of a chemical present in a solid is equivalent to ppm.

Sodium Dithionite ($Na_2S_2O_4$) Injection at R-42 on August 24-25, 2017

Injection of 9,000 gallons of raw R-42 water containing 350 kg of sodium dithionite ($Na_2S_2O_4$) and 245 kg of sodium sulfite (Na_2SO_3) to buffer the solution. 1,000 gallons of potable water were injected after the amendment, reacted for three days, and removed by pumping R-42.

Molasses Injection at R-28 on September 9, 2017

Injection of 30,000 gallons of raw R-28 water with 3.3 weight percent of molasses (33 g/kg). 1,500 gallons of potable water, containing 10 vol% ethanol, were injected after the molasses. No additional pumping immediately followed to remove molasses.

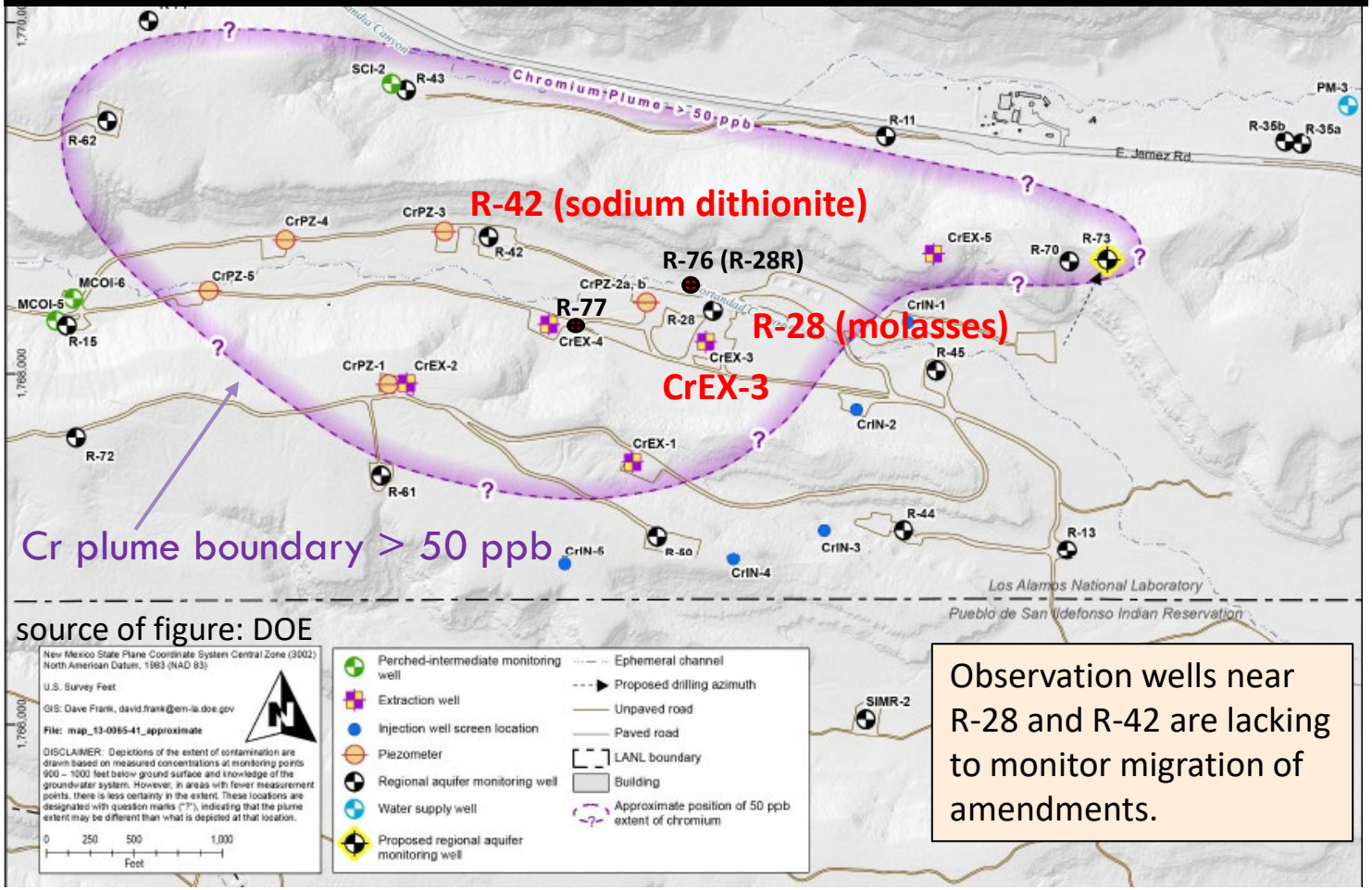
5 IM injection wells (blue)

5 IM extraction wells (purple/yellow)

PM-3 (light blue)

22 regional aquifer monitoring wells (tan and black)

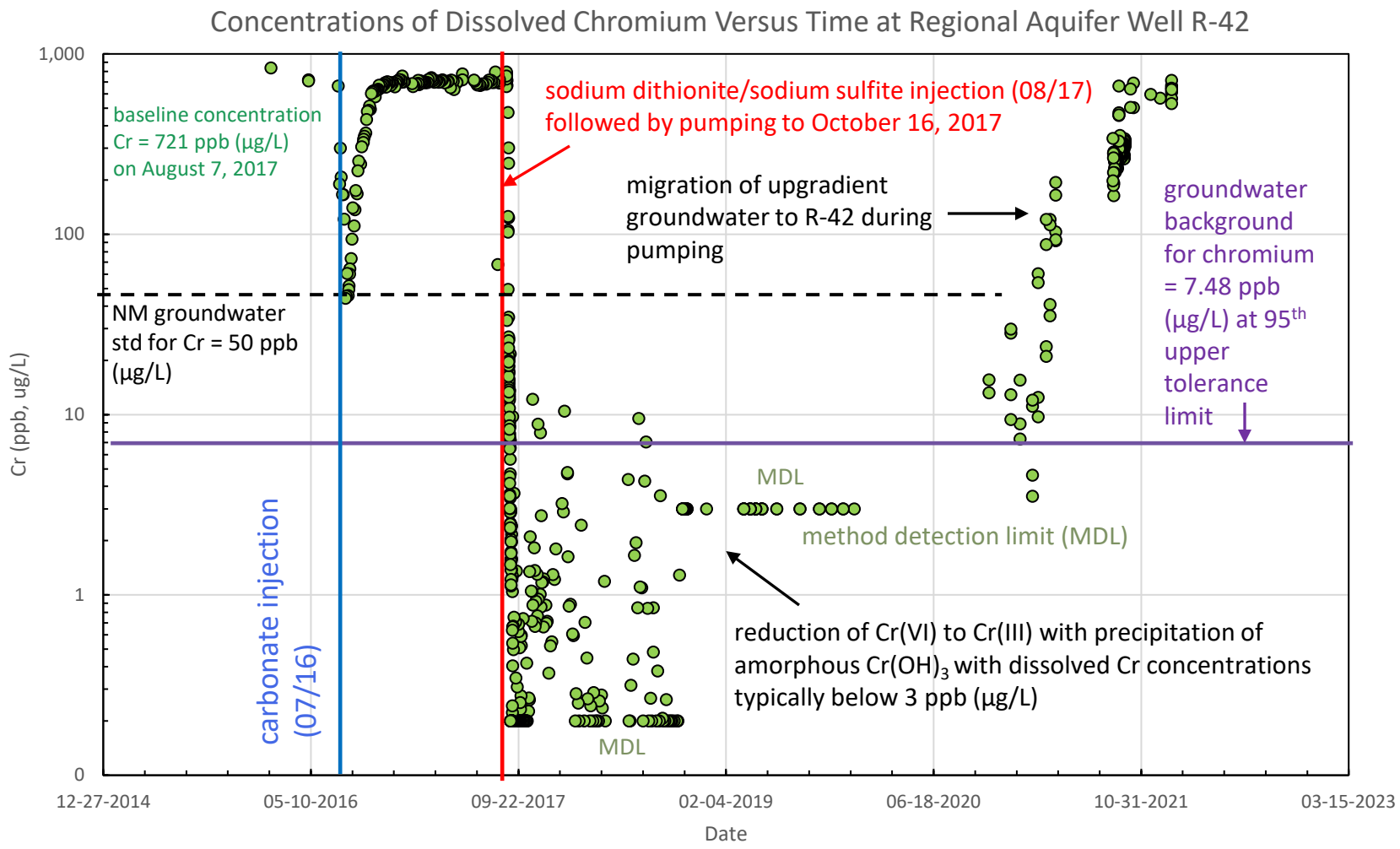
4 perched zone (vadose zone) monitoring wells (green)



source of figure: DOE

Observation wells near R-28 and R-42 are lacking to monitor migration of amendments.

Concentrations of Dissolved Chromium (Cr) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)



Summary of Groundwater Remediation at R-42

- Chromate has been reduced to chromium(III) at regional well R-42 by injection of sodium dithionite and sodium sulfite between 2017 and 2021.
- Chromium concentrations at R-42 typically exceed 600 ppb (µg/L) in early 2022. The well is generally providing chemical data representative of pre-amendment conditions.
- The volume of remediated groundwater and aquifer material is not known with certainty in the absence of observation wells near R-42.
- NMED is requiring DOE to investigate nature and extent of iron and manganese released to groundwater from sodium dithionite injection at R-42.

Biogeochemistry Overview of the Regional Aquifer at LANL

- Groundwater in the regional aquifer is oxic, having measurable dissolved oxygen typically ranging from 5 to 8 ppm (mg/L).
- Groundwater in the regional aquifer has pH values typically ranging from 7.5 to 8.5.
- Microbes consist of aerobic, anaerobic, and facultative bacteria, which switch back and forth between aerobic and anaerobic populations.
- Diverse populations of aerobic, anaerobic, and facultative bacteria occur in groundwater in the regional aquifer and are also attached to aquifer solids as biofilms.

Biogeochemistry Overview of the Regional Aquifer at LANL

- Aerobic bacteria biosynthesize dissolved oxygen for cell growth.
- Anaerobic bacteria, in the absence of dissolved oxygen, biosynthesize nitrate, manganese, chromium, iron, sulfur, and inorganic and organic carbon for cell growth.
- Anaerobic bacteria are stimulated by consuming organic carbon and utilizing other redox-sensitive chemicals (nitrogen, manganese, iron, and sulfur) in the absence of dissolved oxygen.

Sodium Dithionite ($Na_2S_2O_4$) Injection at R-42 on August 24-25, 2017

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Molasses Injection at R-28 on September 9, 2017

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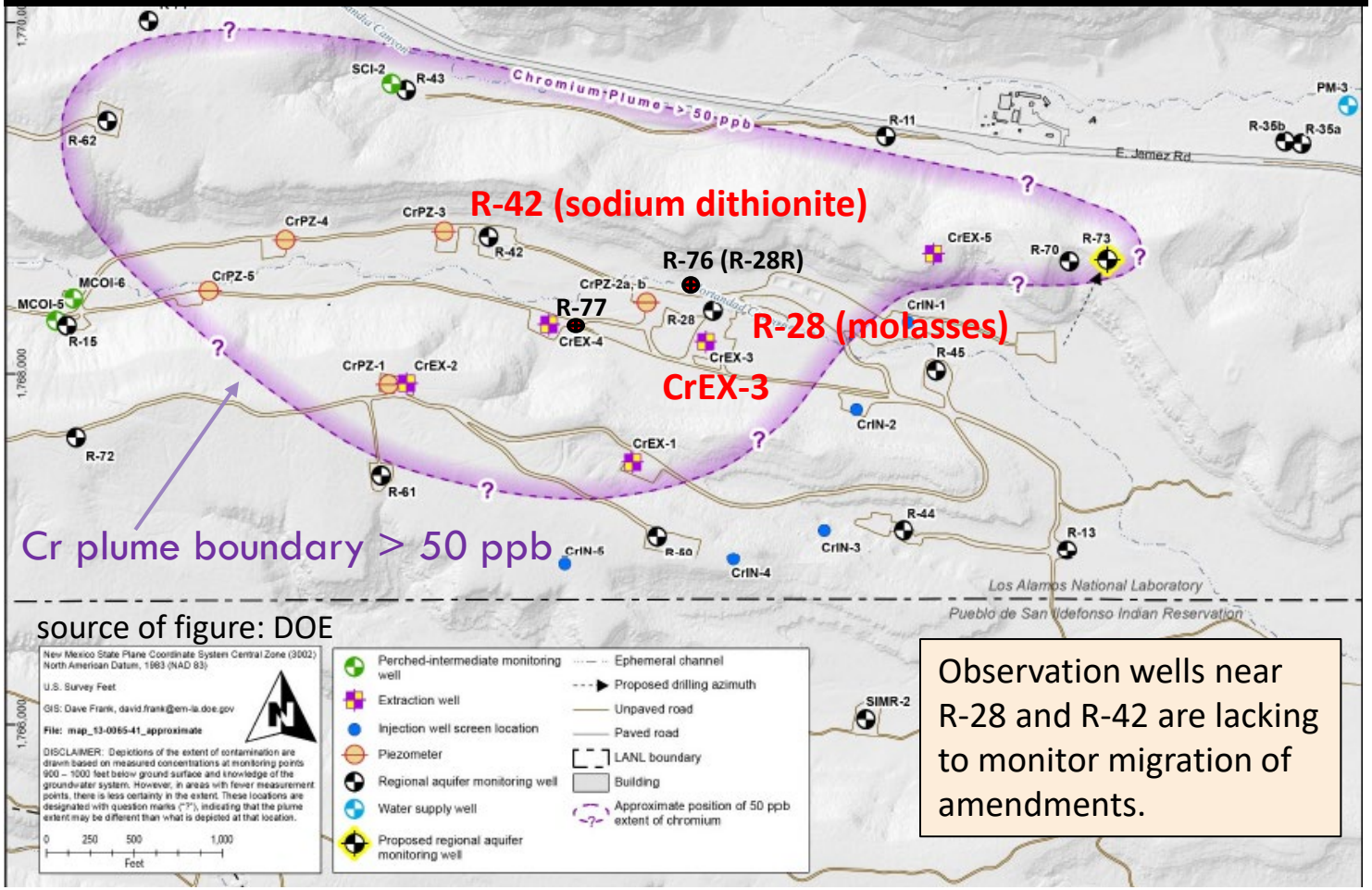


Observation wells near R-28 and R-42 are lacking to monitor migration of amendments.

Molasses Chemistry

Molasses is a viscous product resulting from refining sugar cane or sugar beets into complex sugars ($C_{12}H_{22}O_{11}$).

Generic Composition of Sugar Cane Molasses

Element	Concentration (mg/kg, ppm) [wt. %]
Total Soluble Solids	219,000 [21.9]
Reducing Sugars	178,000 [17.8]
Total Sugars	499,000 [49.9]
Sucrose	321,000 [32.1]
pH	5.6
Energy	12,130 kilojoules/kg (2,899 kilocalories/kg)

parts per million is ppm, kilogram is kg

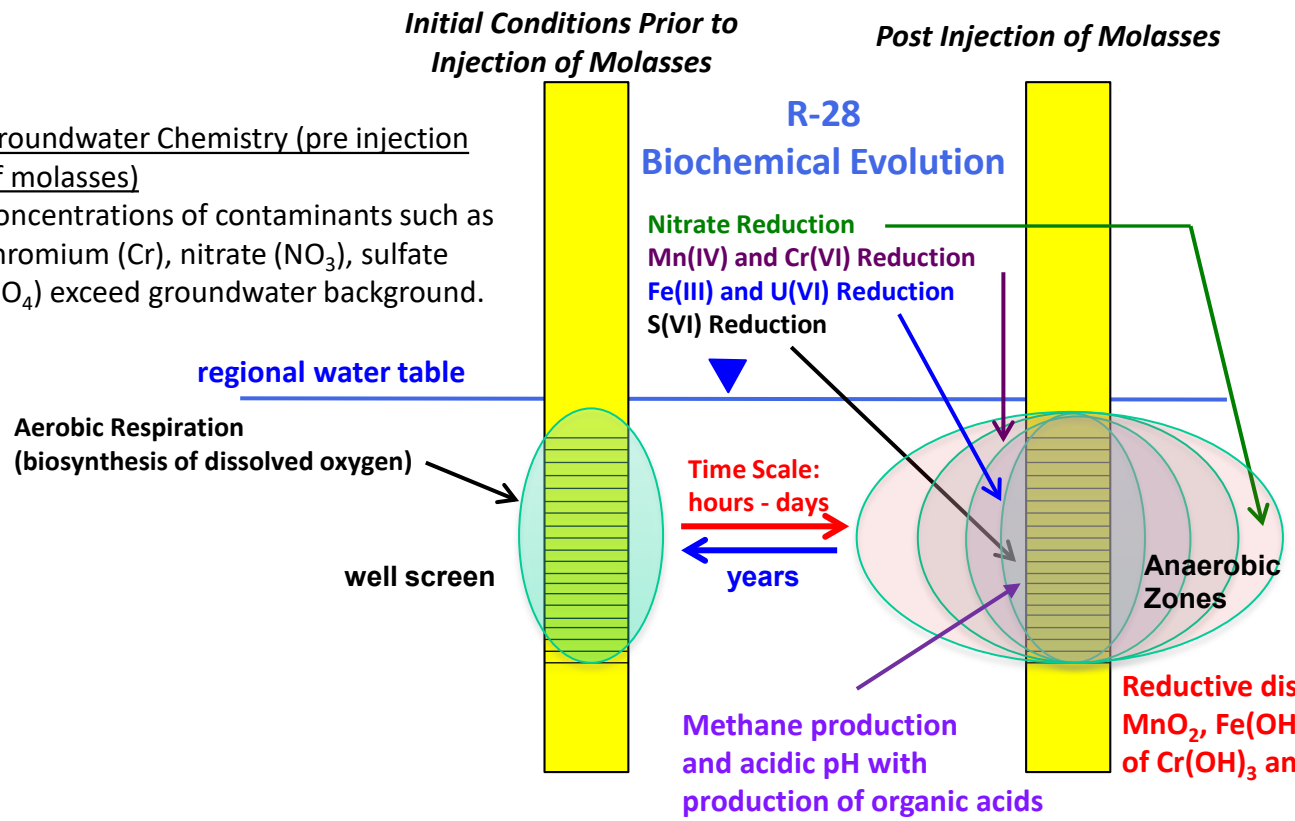
Organic Acids Present in Sugarcane Molasses (Nelson 1929 and Olbrich 1963)

Generic Acid Composition

Acid	Concentration (mg/kg, ppm)
Acetic	2,000
Aconitic	8,000
Formic	1,000
Glutamic	34,000
Lactic	500

parts per million is ppm, kilogram is kg

Conceptual Model of Molasses Biogeochemistry at Well R-28



Groundwater Chemistry (pre injection of molasses)

Concentrations of contaminants such as chromium (Cr), nitrate (NO_3), sulfate (SO_4) exceed groundwater background.

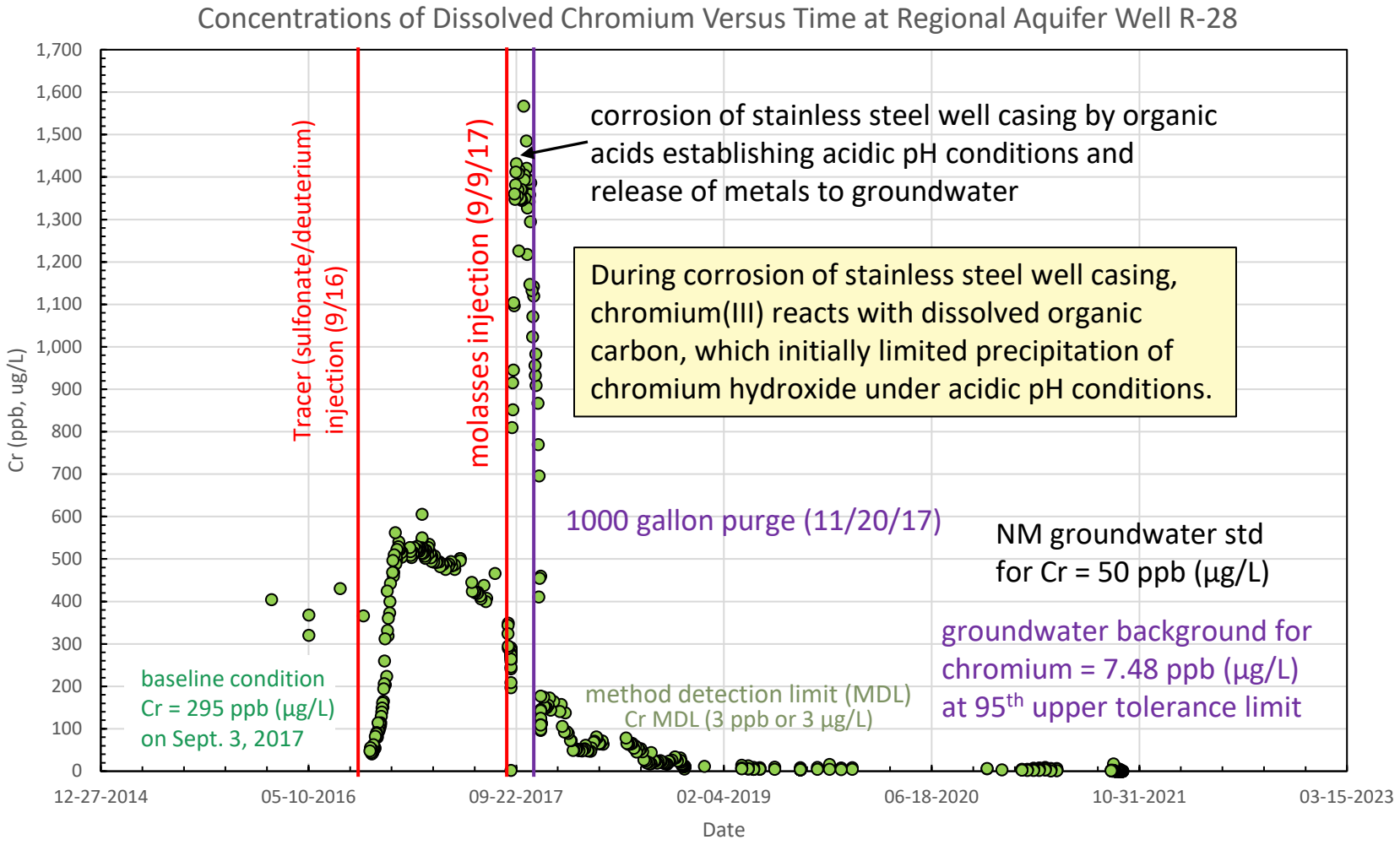
Groundwater Chemistry (post injection of molasses)

Above baseline concentrations of iron (Fe), manganese (Mn), total organic carbon (TOC), organic nitrogen, total carbonate alkalinity, and total dissolved solids (TDS) with acidic pH.

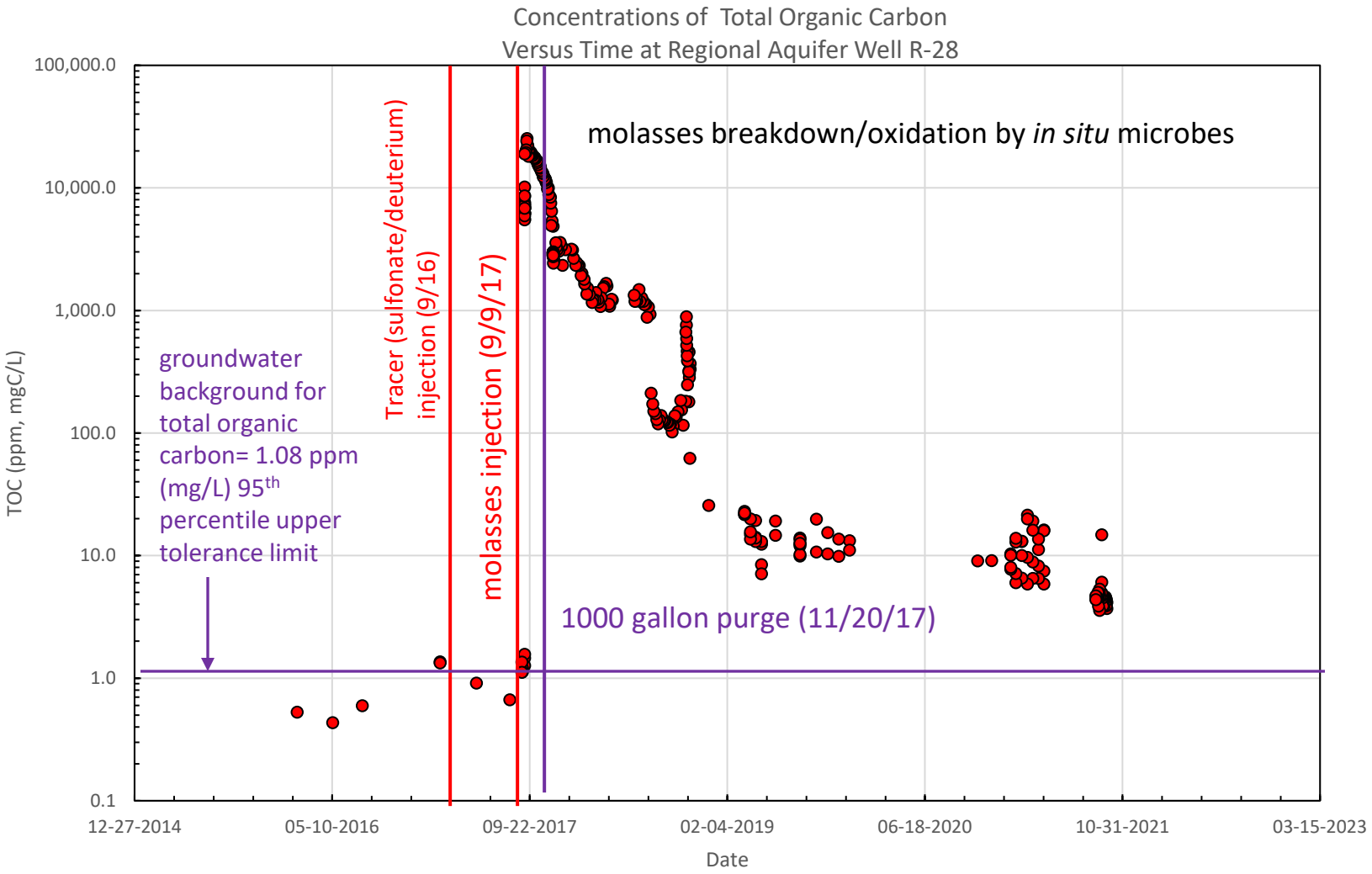
Concentrations of contaminants such as chromium (Cr), nitrate (NO_3), uranium (U) are within groundwater background.

Generation of hydrogen sulfide and methane and biomass with residual molasses and other forms of dissolved and suspended organic matter produce biofouling.

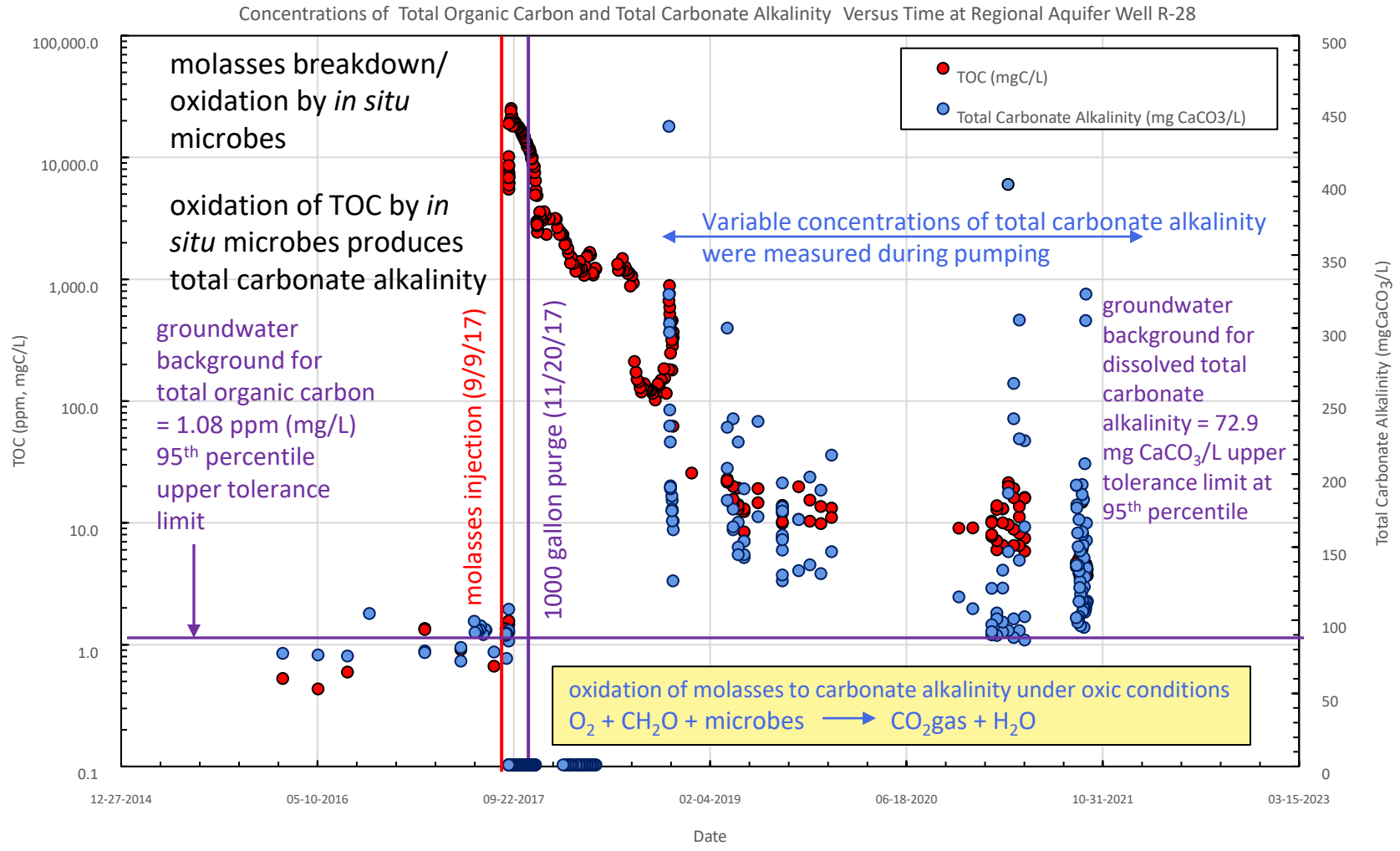
Concentrations of Dissolved Chromium (Cr) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



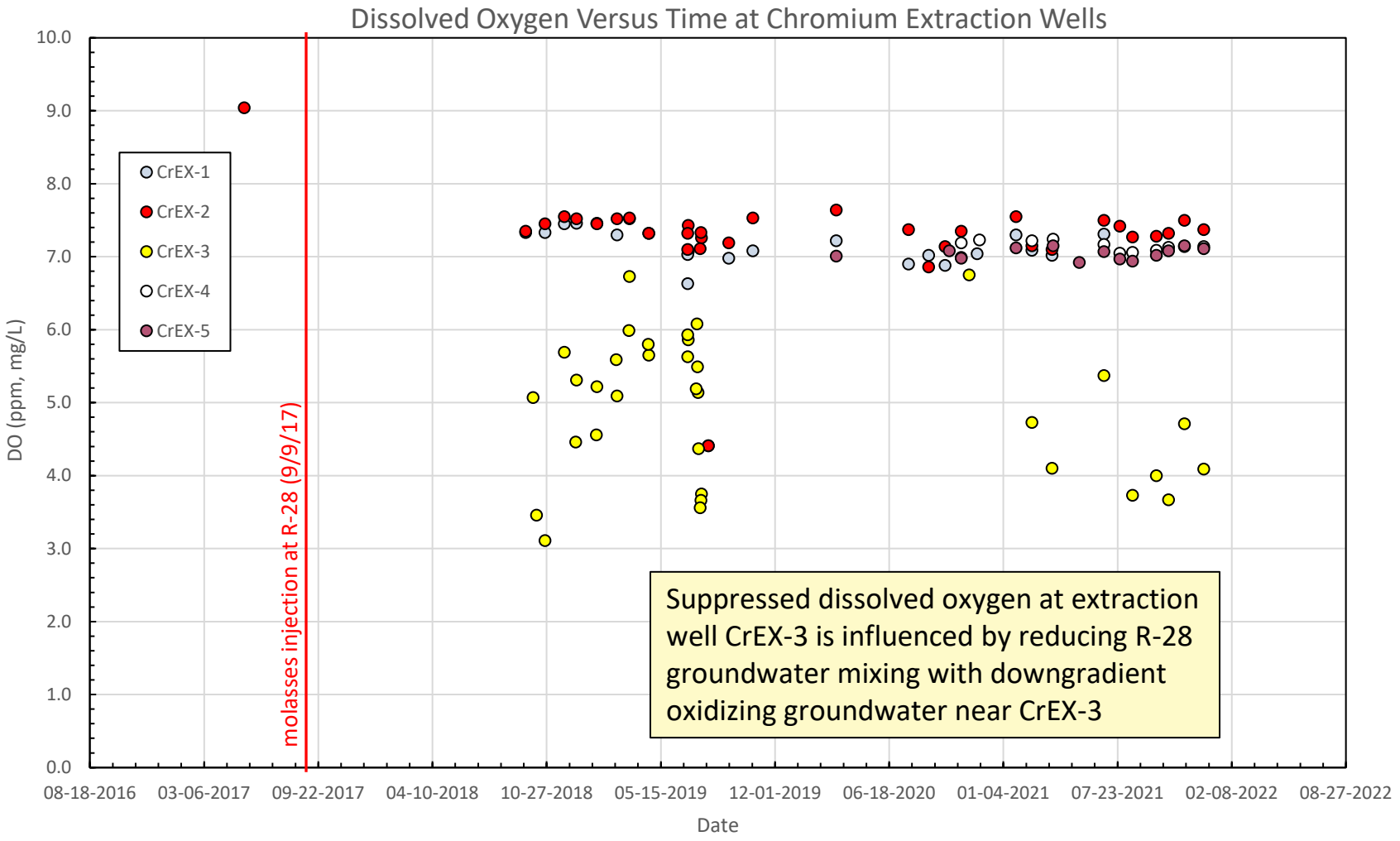
Concentrations of Total Organic Carbon Versus Time at Regional Aquifer Well R-28



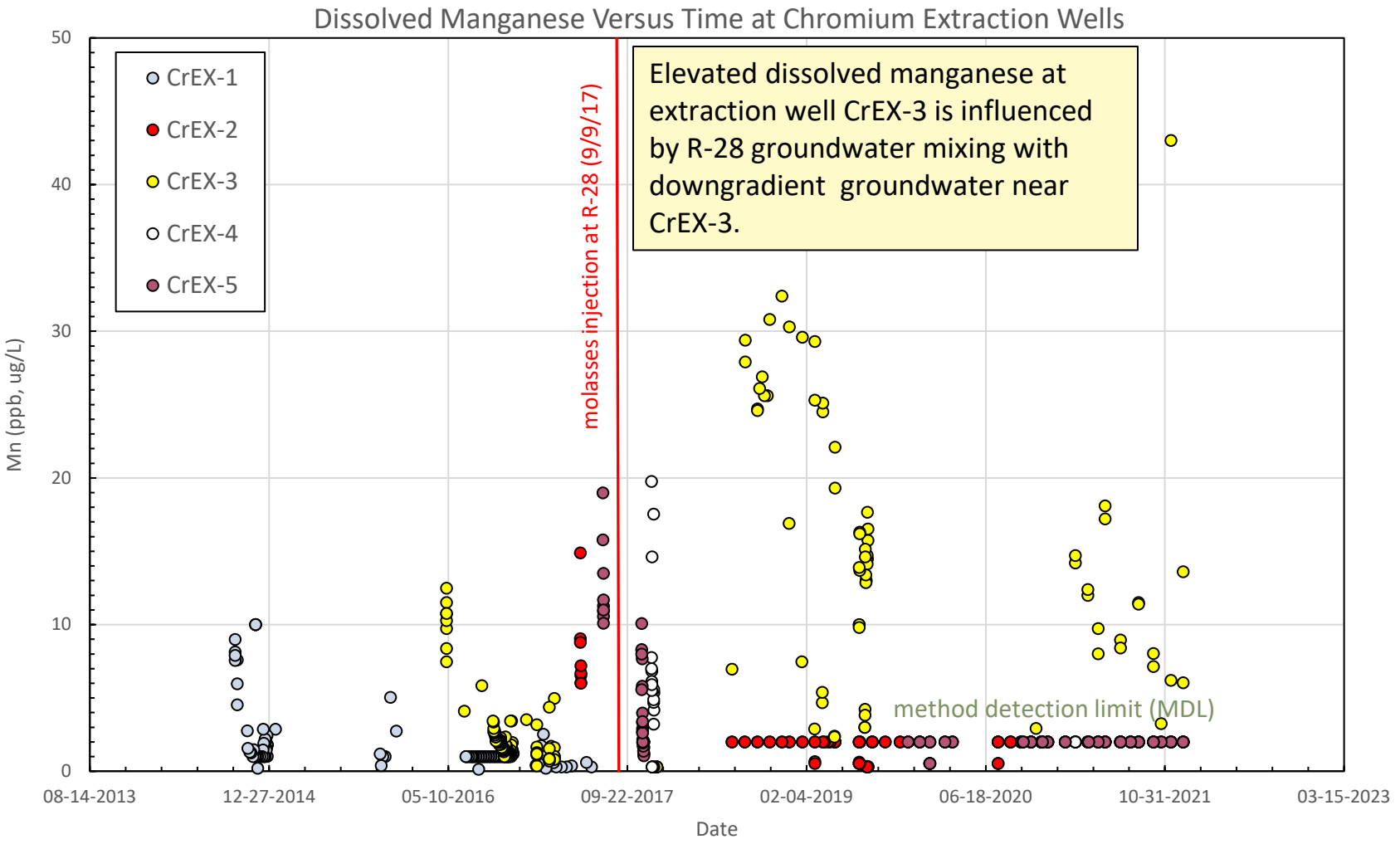
Concentrations of Total Organic Carbon and Total Carbonate Alkalinity Versus Time at Regional Aquifer Well R-28



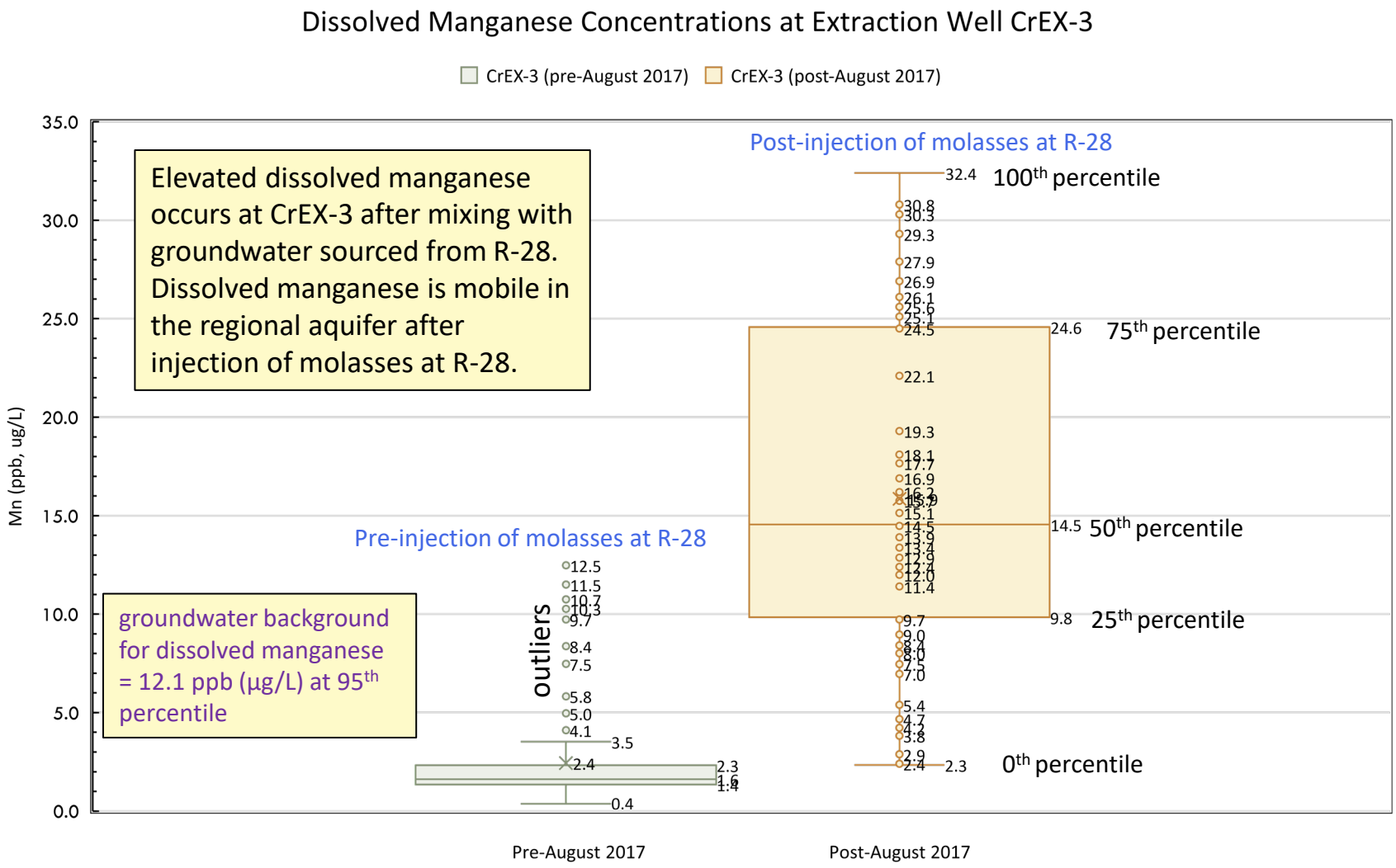
Dissolved Oxygen Versus Times at Chromium Extraction Wells



Dissolved Manganese Versus Times at Chromium Extraction Wells



Dissolved Manganese Concentrations at Extraction Well CrEX-3 Before and After Molasses Injection at R-28



Summary of Groundwater Remediation at R-28

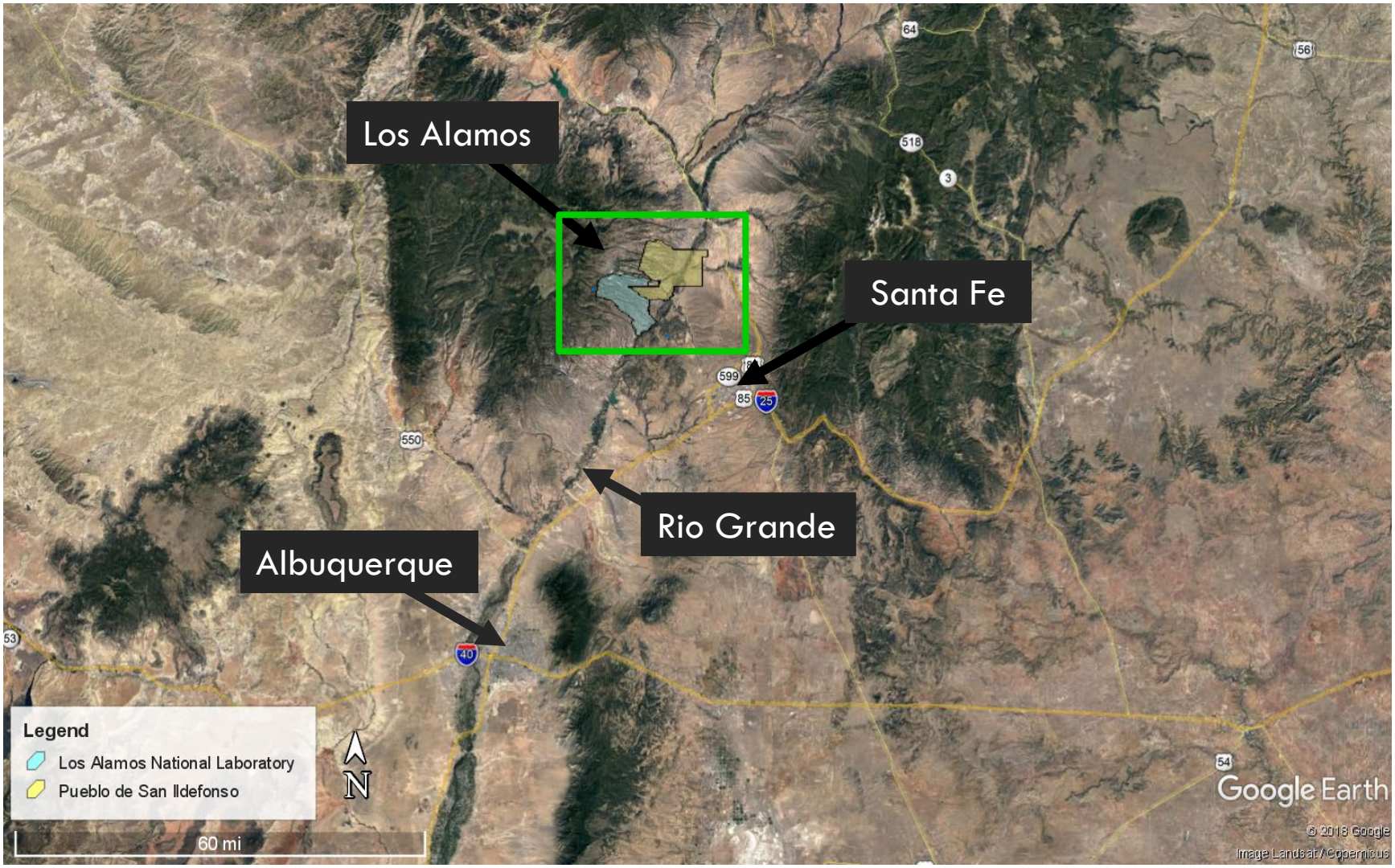
- At regional well R-28, chromate has been reduced to chromium(III) by oxidation of reactive organic carbon (molasses) during consumption by *in situ* bacteria (aerobic, anaerobic, and facultative).
- Oxidation and consumption of molasses by *in situ* bacteria initially produced organic acids that decreased groundwater pH as low as 4.6. This caused corrosion of stainless-steel well casing with secondary release of chromium, iron, manganese, other metals to groundwater.
- Residual organic matter/biomass and biofilms have created reactive biogeochemical conditions that render R-28 useless in providing representative geochemical and hydraulic data and information. The well will be replaced by a new well (R-76) in 2022 - 2023.
- Molasses injection at R-28 indirectly impacted extraction well CrEX-3 by mobilizing iron, manganese, dissolved organic carbon, and other chemicals.

Path Forward

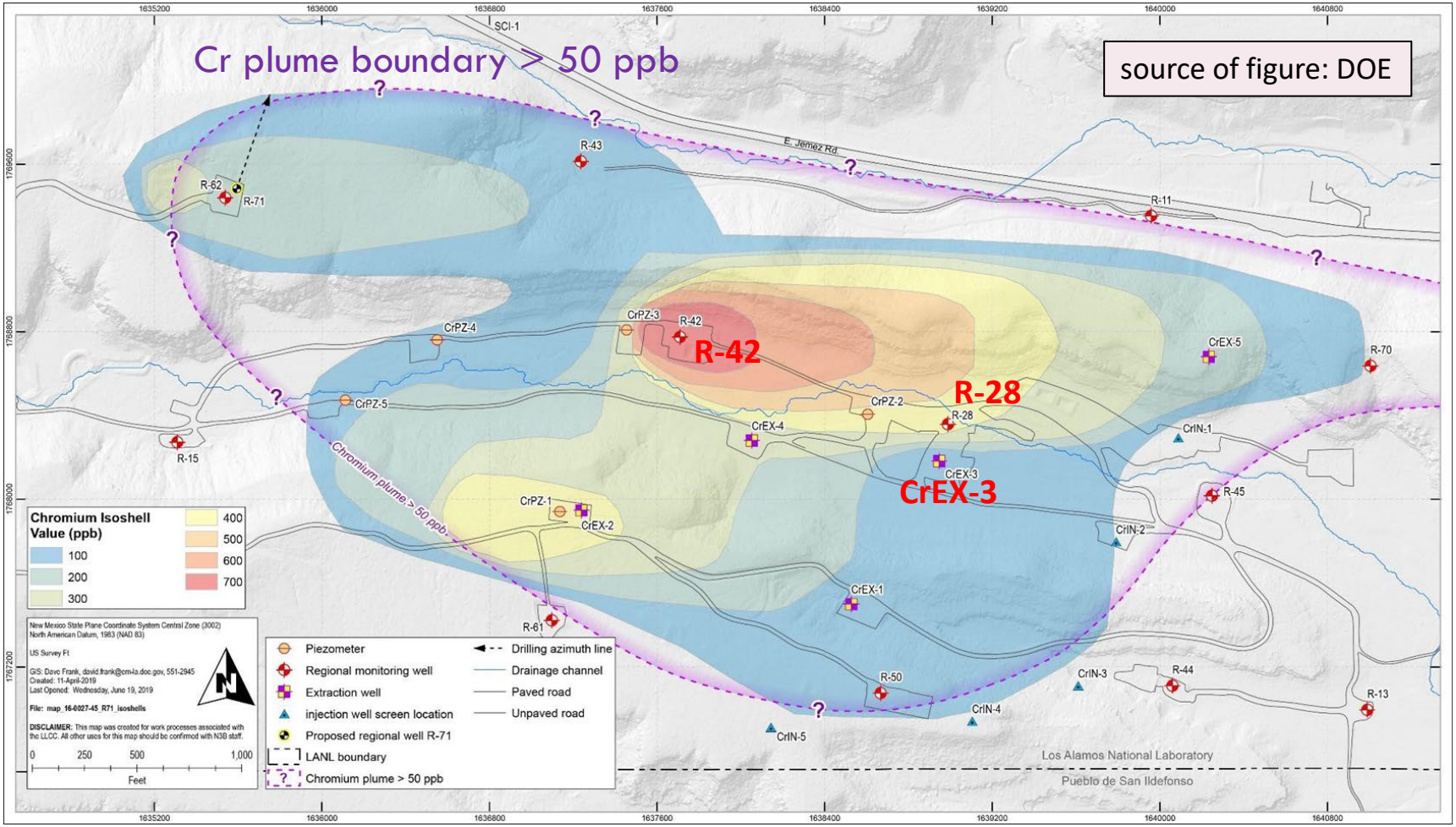
- NMED and DOE concur that R-28 does not provide technically defensible groundwater monitoring data and information. A replacement well (R-76) will be drilled in 2022 - 2023.
- Regional aquifer well R-42 is currently being evaluated by NMED and DOE for providing reliable data and information representative of pre-injection of chemicals.
- Site-specific hydrogeological and geochemical conditions are not conducive for using biogeochemical amendments (sodium dithionite and molasses) to remediate the chromium plume at LANL. Pump and treat is the preferred remediation technology.
- Additional characterization on the nature and extent of the chromium plume (lateral and vertical) is required to successfully remediate the chromium plume in the regional aquifer.

Supplemental Material

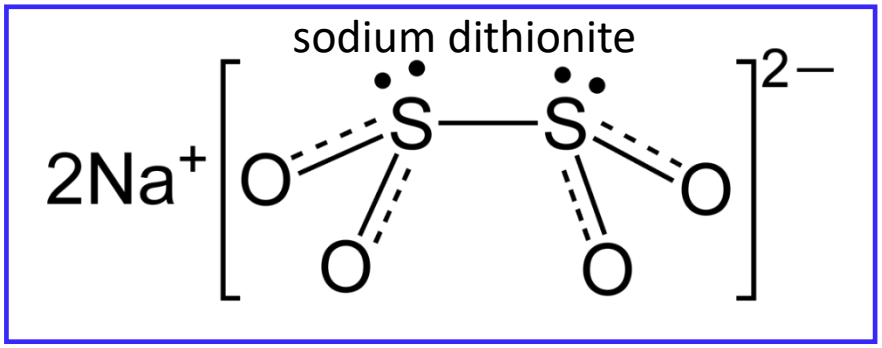
Los Alamos National Laboratory and Surrounding Area, North Central New Mexico

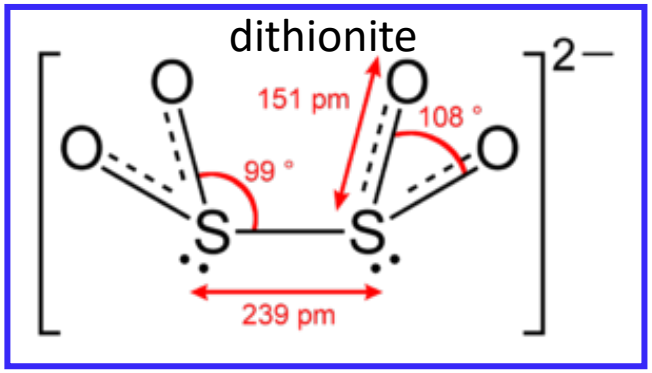


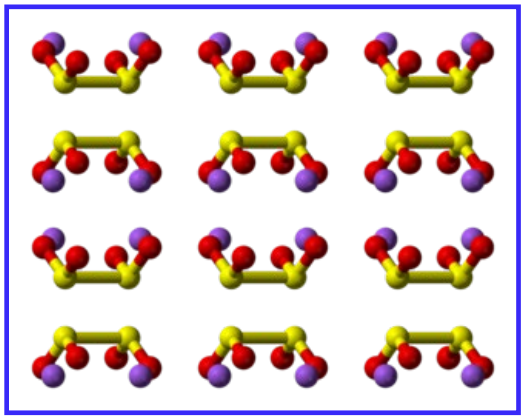
Chromium Plume Detail – Coalesced Plumes



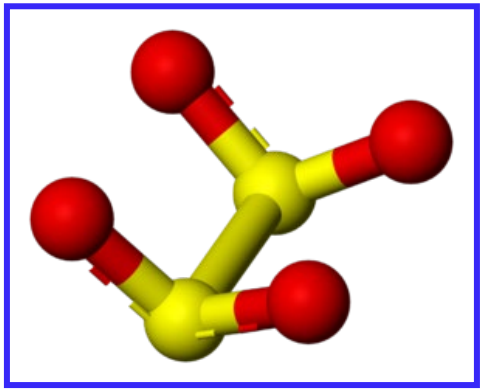
Sodium Dithionite and Reaction Sequence for Iron and Chromium







Sulfur atoms are shown in yellow. Sodium atoms are shown in purple. Oxygen atoms are shown in red.



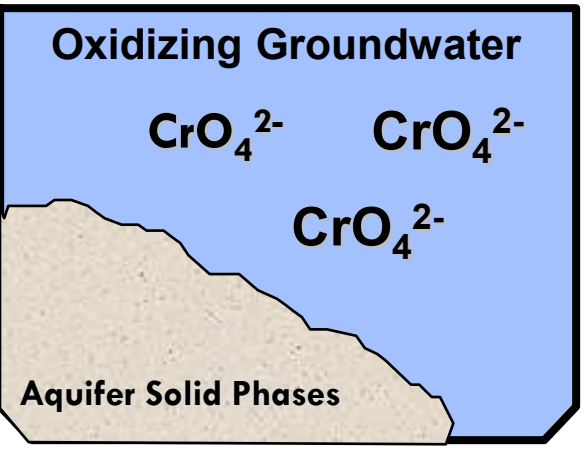
A: $Na_2S_2O_4 = 2Na^+ + 2SO^{\bullet}{}_2^-$ (sodium dithionite dissociates to sodium cation and sulfoxyl radical)

B: $SO^{\bullet}{}_2^- + Fe^{3+} + H_2O = SO_3^{2-} + Fe^{2+} + 2H^+$ (sulfoxyl radical oxidizes to sulfite and reduces ferric iron to ferrous iron; sulfite oxidizes to sulfate and produces acidic conditions)

C: $3Fe^{2+} + 5H^+ + CrO_4^{2-} = 3Fe^{3+} + Cr(OH)_3 + H_2O$ (ferrous iron reduces chromate to chromium[III])

PHREEQC Batch Model of Chromium Reduction by Sodium Dithionite ($Na_2S_2O_4$) and Sodium Sulfite (Na_2SO_3) at Regional Aquifer Well R-42

R-42 sampled May 6, 2016



pH = 7.46

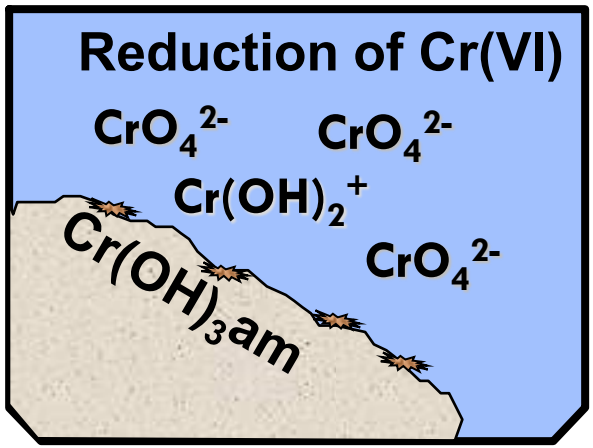
$Cr_{dissolved}$ = 718 ppb

$Fe_{dissolved}$ = 15 ppb

$Cr(OH)_3am$ (solid)

ppb = parts per billion

$Na_2S_2O_4$ (10,446 ppm) and Na_2SO_3 (7,563 ppm) (0.06 molal)

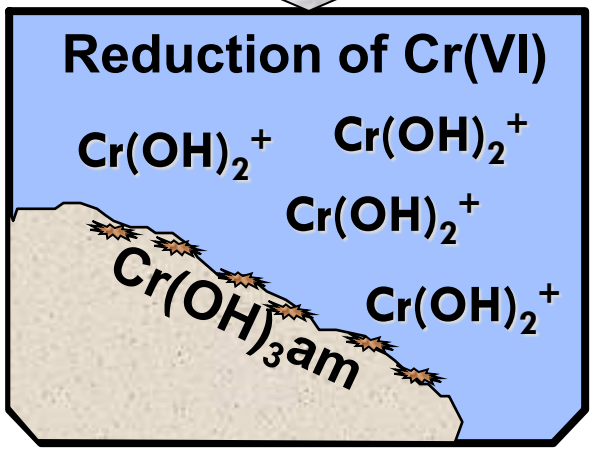


pH = 6.20

$Cr_{dissolved}$ = 75.1 ppb

$Cr(OH)_3am$ = 643 ppb precipitates

$Na_2S_2O_4$ - Na_2SO_3 and $NaHCO_3$(5,040 ppm) - Na_2CO_3 (6,359 ppm) (0.06 molal)

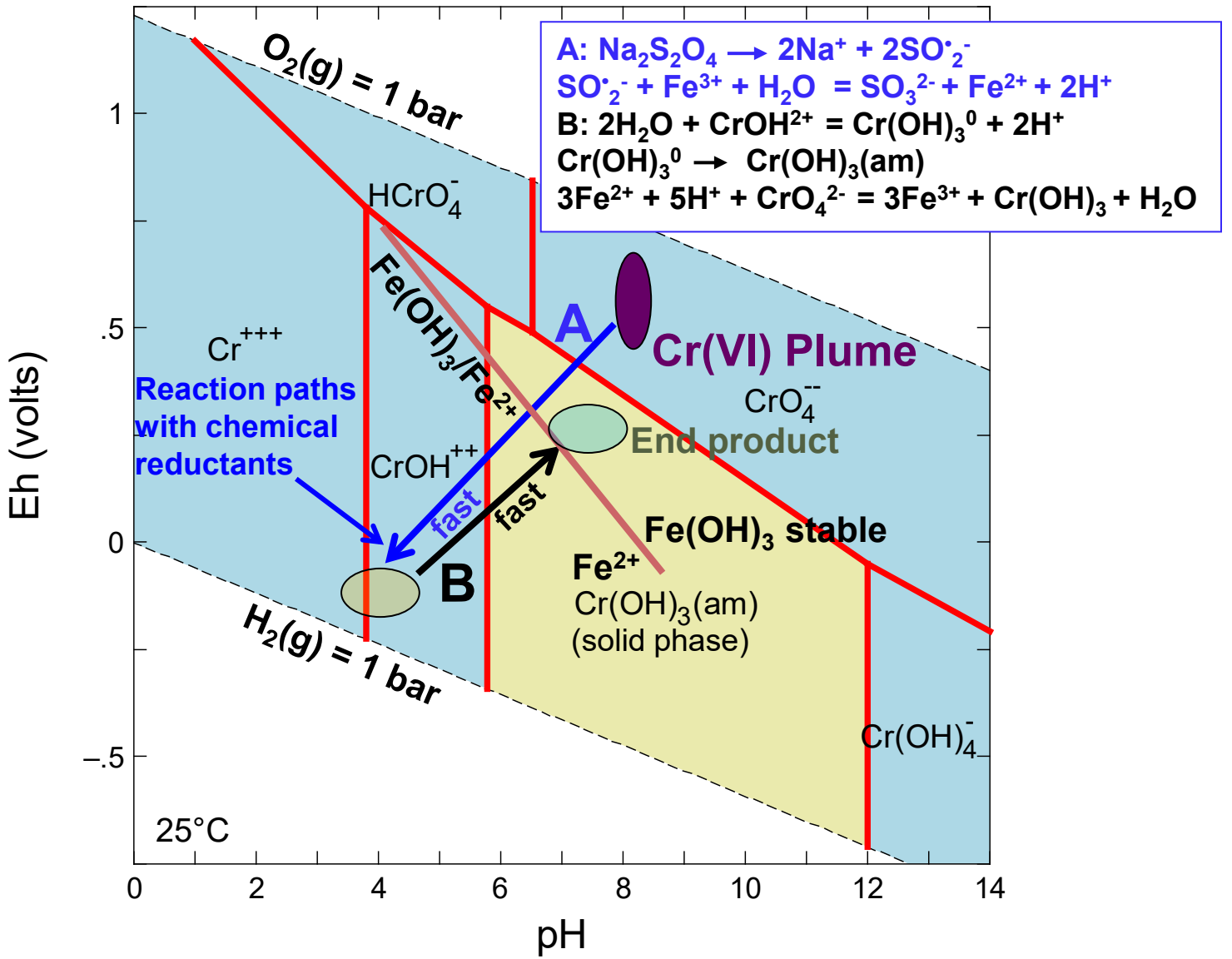


pH = 7.44

$Cr_{dissolved}$ = 1.0 ppb

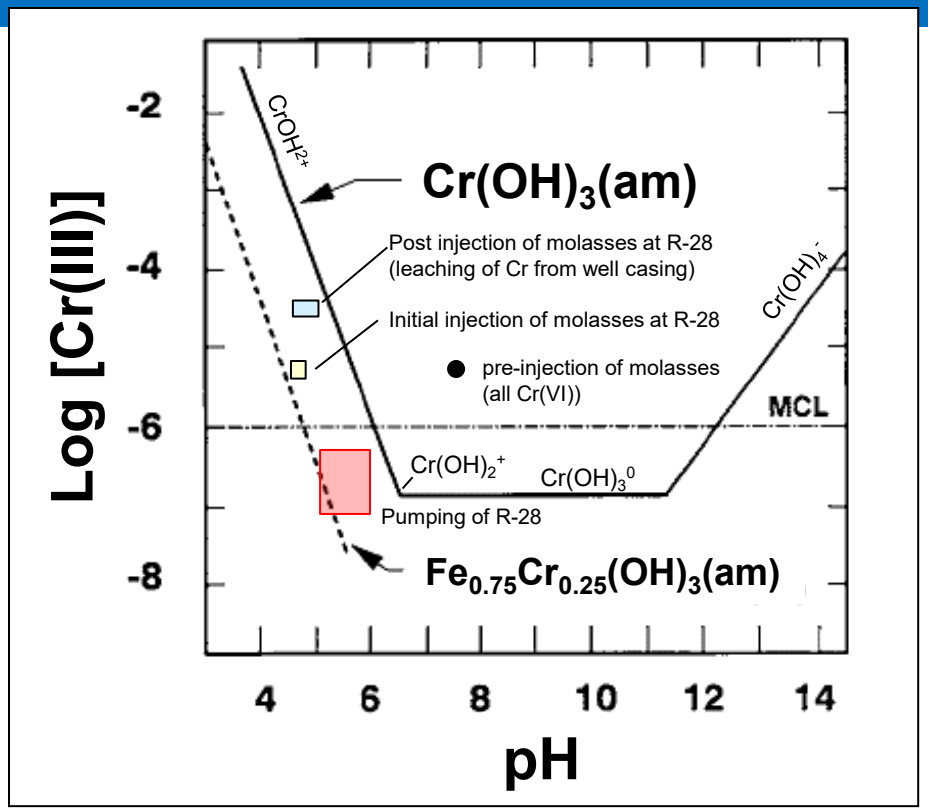
$Cr(OH)_3am$ = 717 ppb precipitates

Eh-pH Diagram for Part of the Cr-O-H System at 25°C and 1 Bar, Total Dissolved Cr = $10^{-4.74}$ Molal



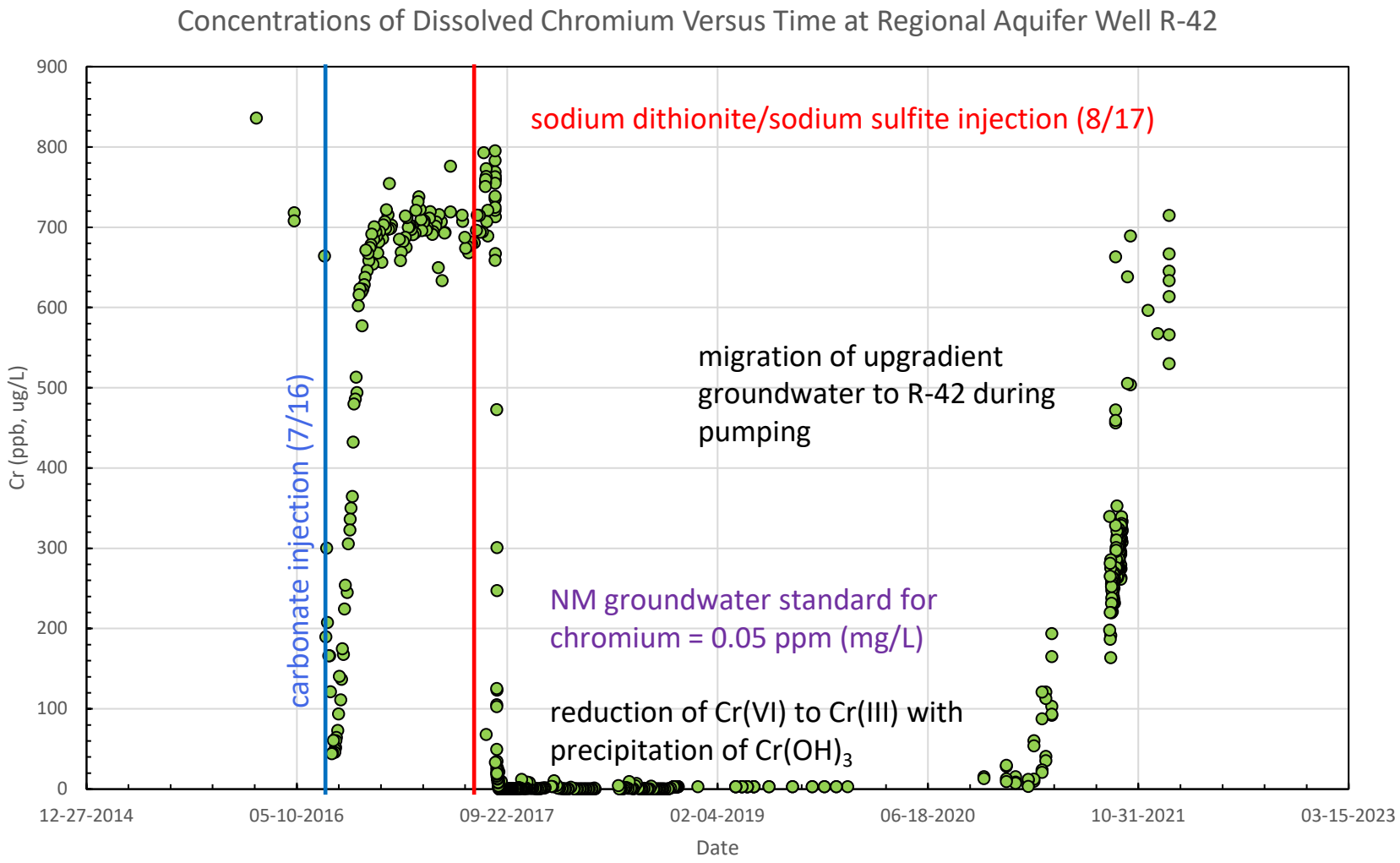
pH Versus Activity of Cr(III) at 25C and 1 Bar (Palmer and Wittbrodt 1991)

09-09-17
09-27-17
10-22-18
-11-02-18

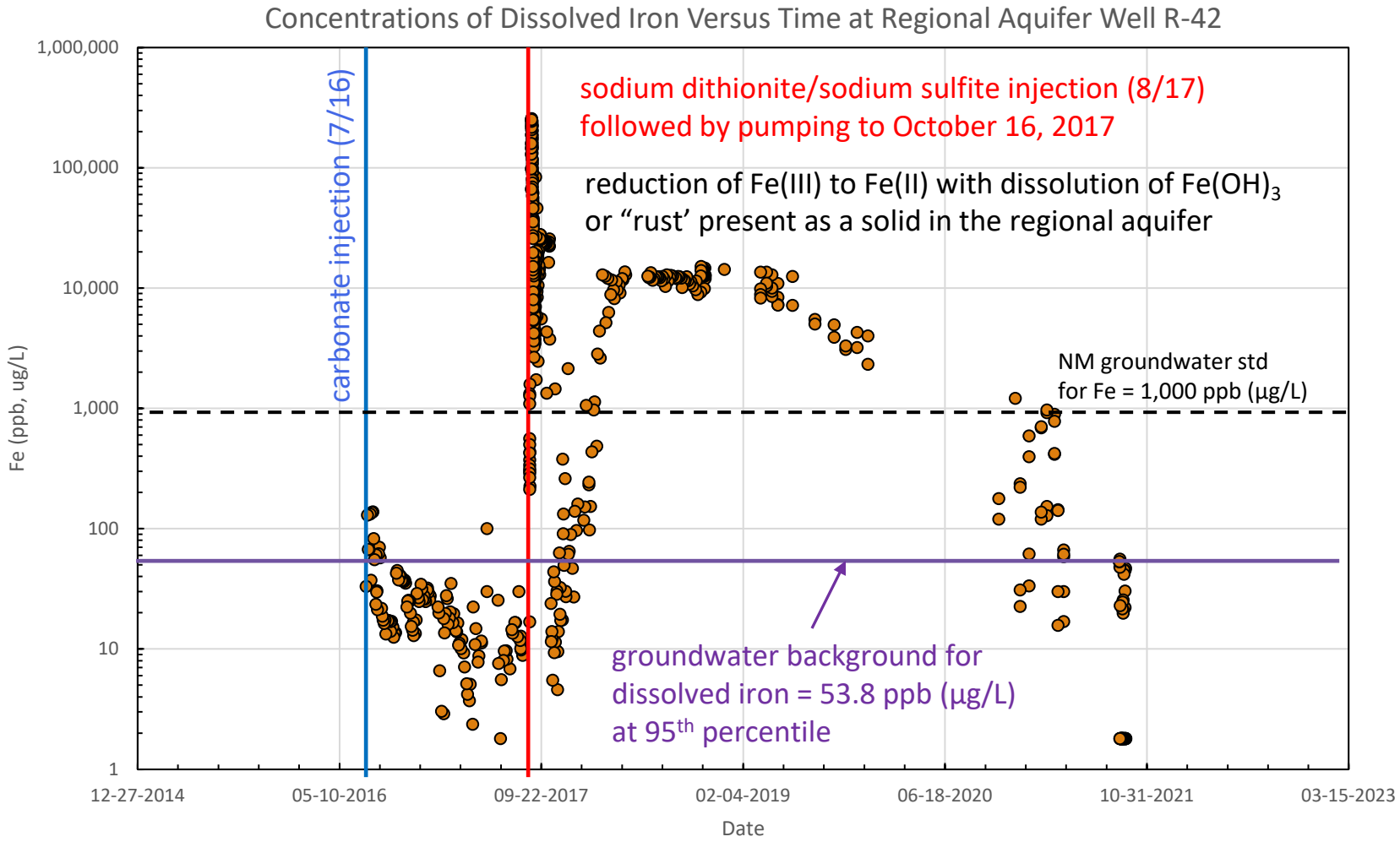


Sources of thermochemical data: Rai et al. 1987 and Sass and Rai 1987

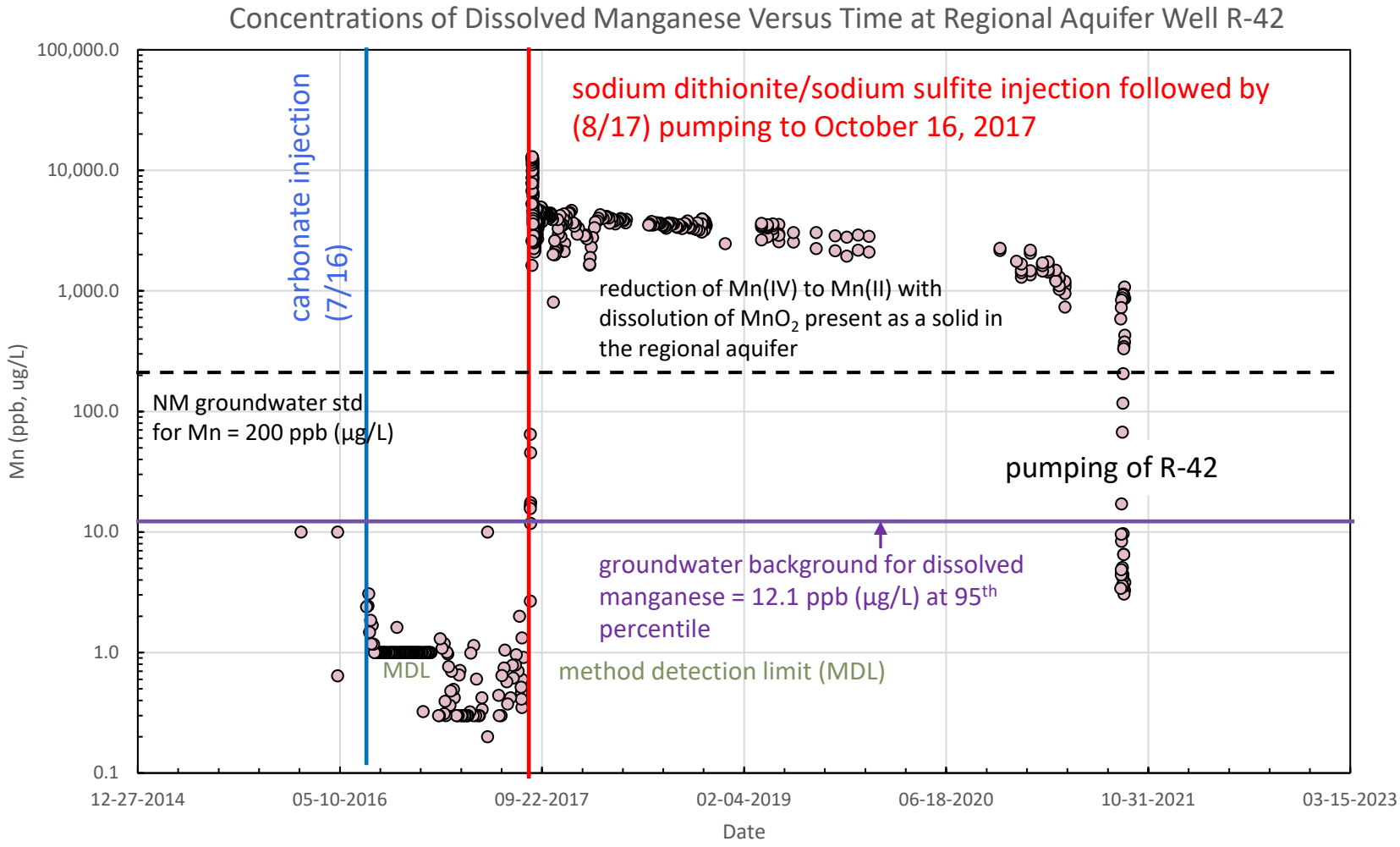
Concentrations of Dissolved Chromium Versus Time at Regional Aquifer Well R-42 (source of data: DOE)



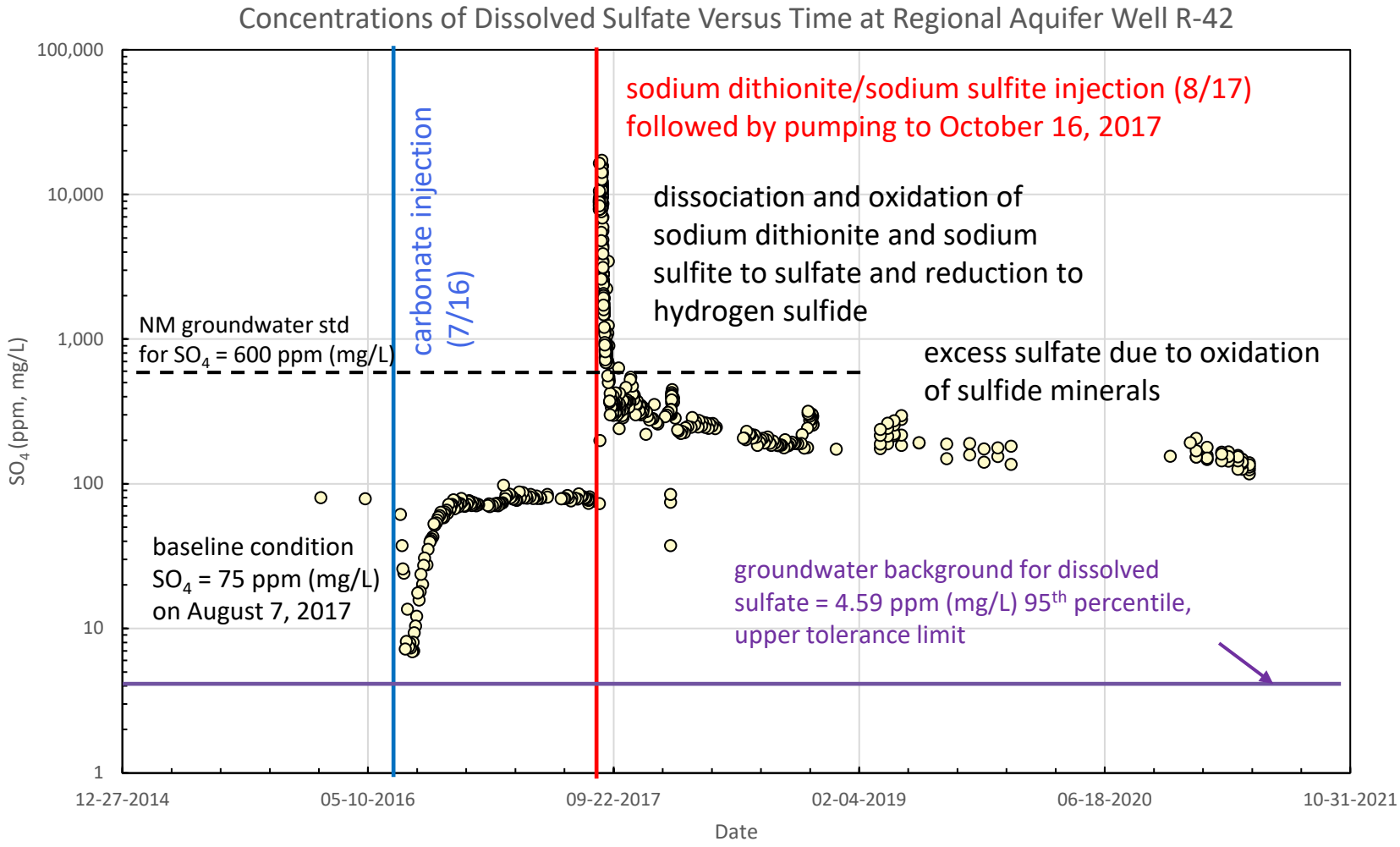
Concentrations of Dissolved Iron (Fe) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)



Concentrations of Dissolved Manganese (Mn) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)



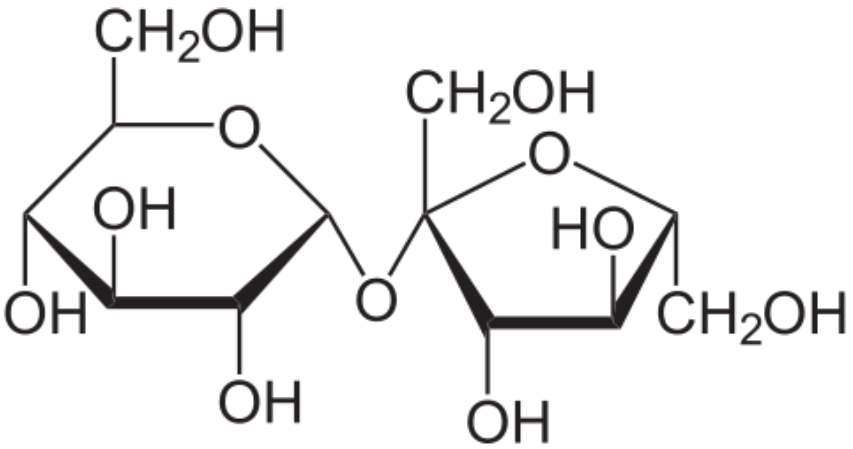
Concentrations of Dissolved Sulfate (SO_4) Versus Time at Regional Aquifer Well R-42 (source of data: DOE)

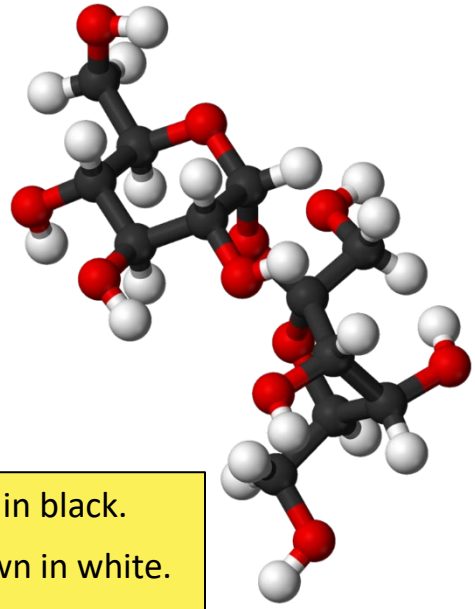


Molasses Chemistry

Molasses is a viscous product resulting from refining sugarcane or sugar beets into complex sugars ($C_{12}H_{22}O_{11}$).

Sucrose (very simple model for molasses)





Carbon atoms are shown in black.

Hydrogen atoms are shown in white.

Oxygen atoms are shown in red.

Molasses Chemistry

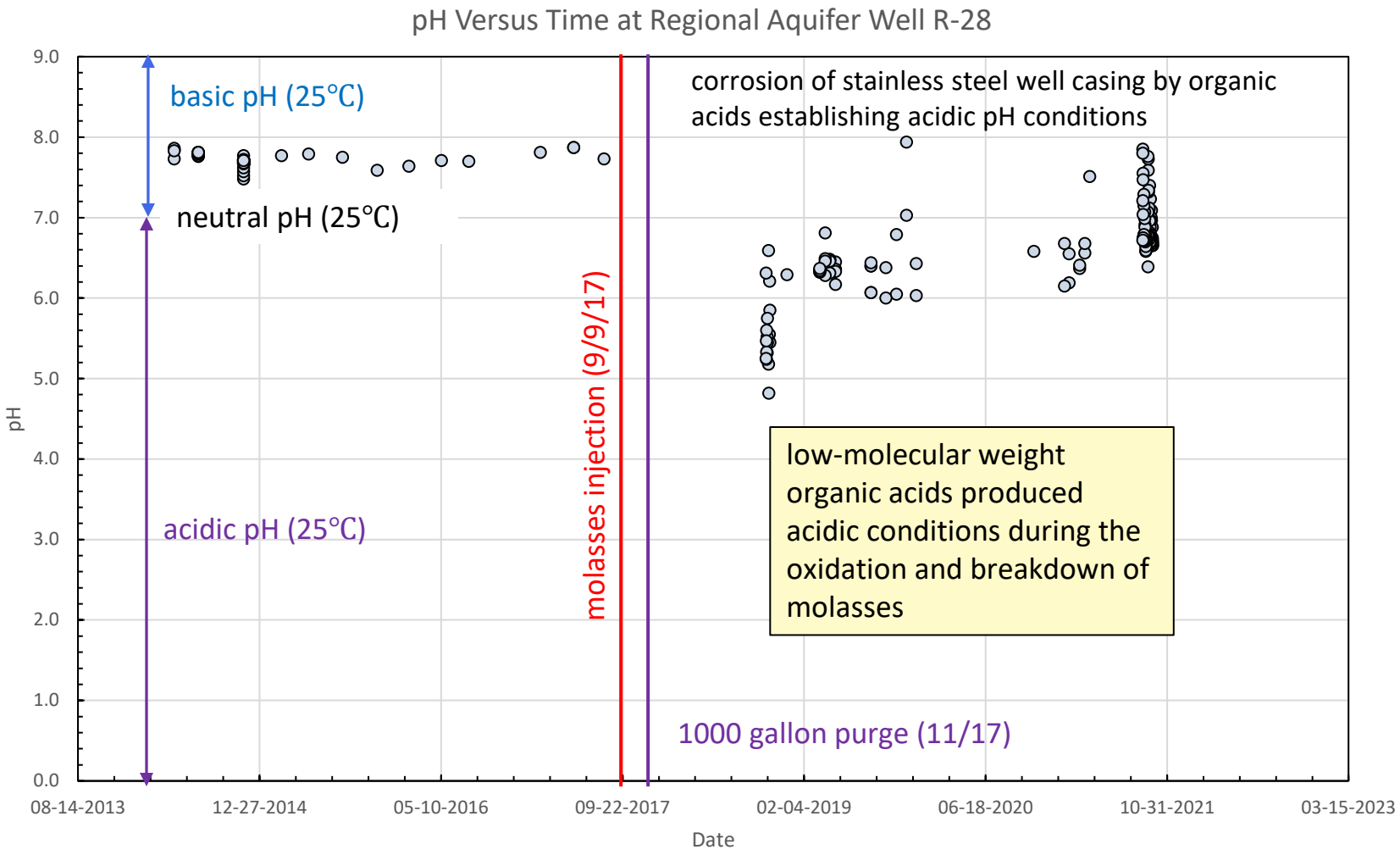
Molasses is a viscous product resulting from refining sugarcane or sugar beets into complex sugars ($C_{12}H_{22}O_{11}$).

Generic Inorganic Composition

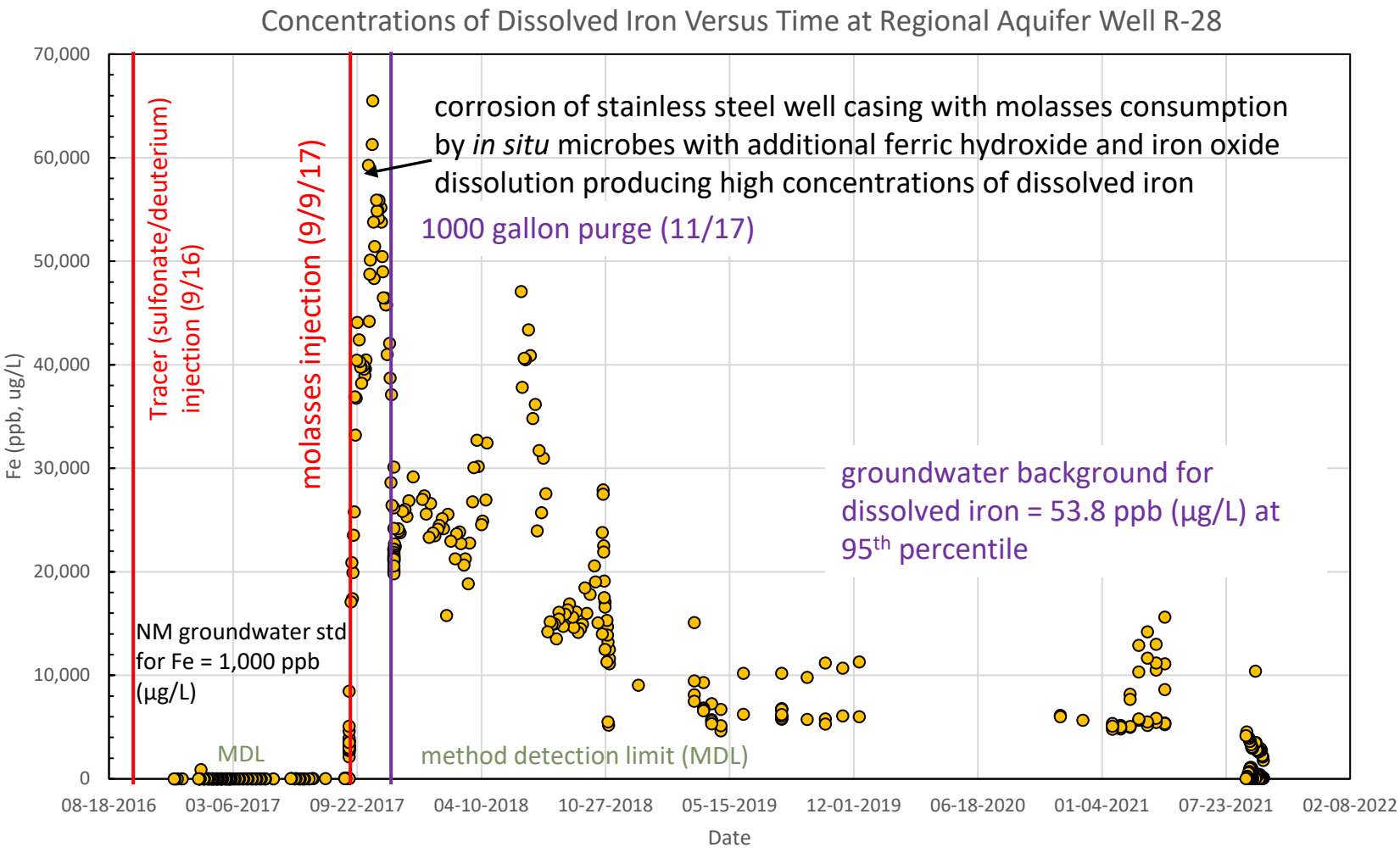
Element	Concentration (mg/kg, ppm)
Calcium	2,050
Iron	47.2
Magnesium	2,420
Manganese	15.3
Phosphorus	310
Potassium	14,640
Sodium	370
Zinc	2.9
H_2O	219,000 (21.9 wt. %)

parts per million is ppm, kilogram is kg

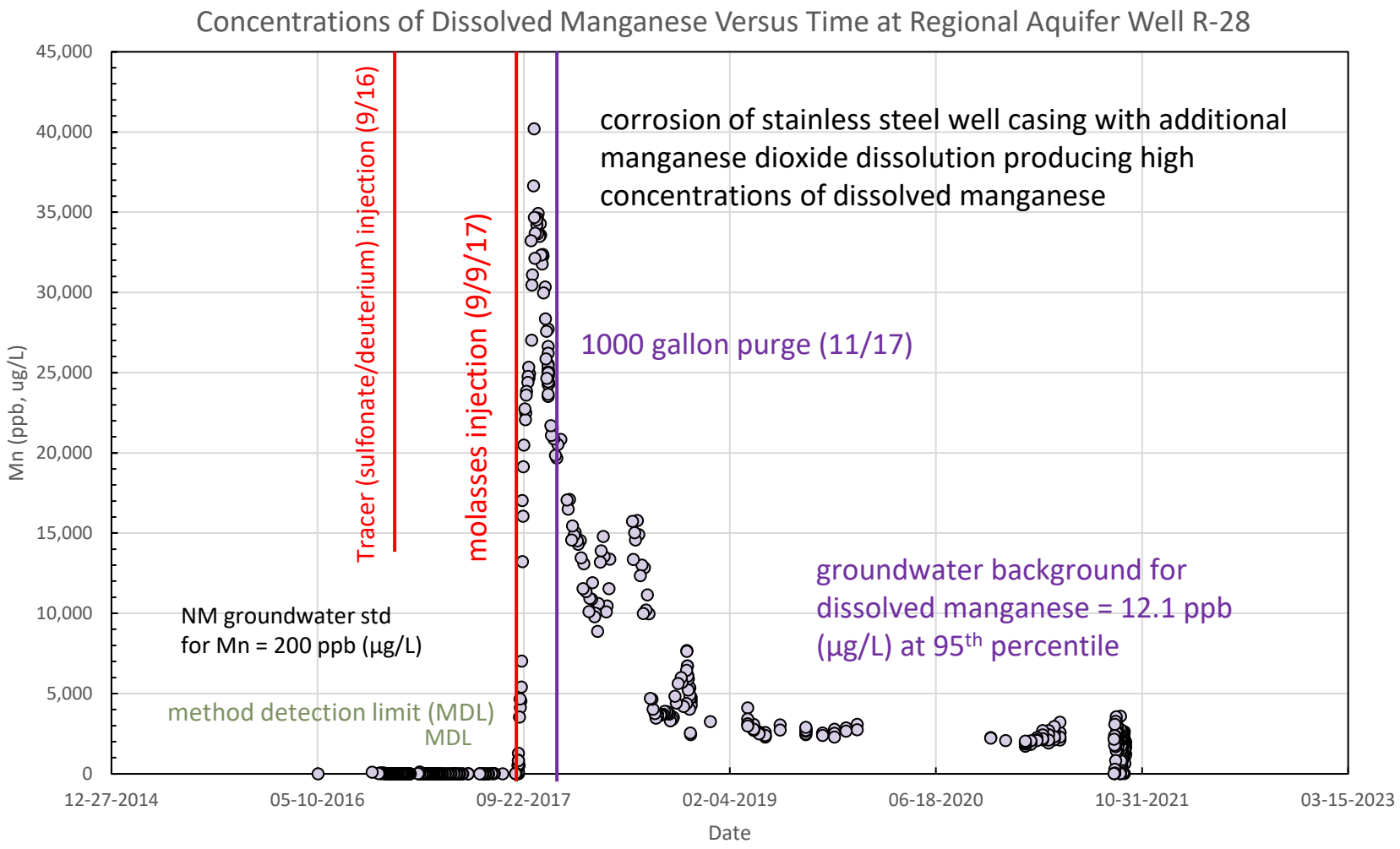
pH Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



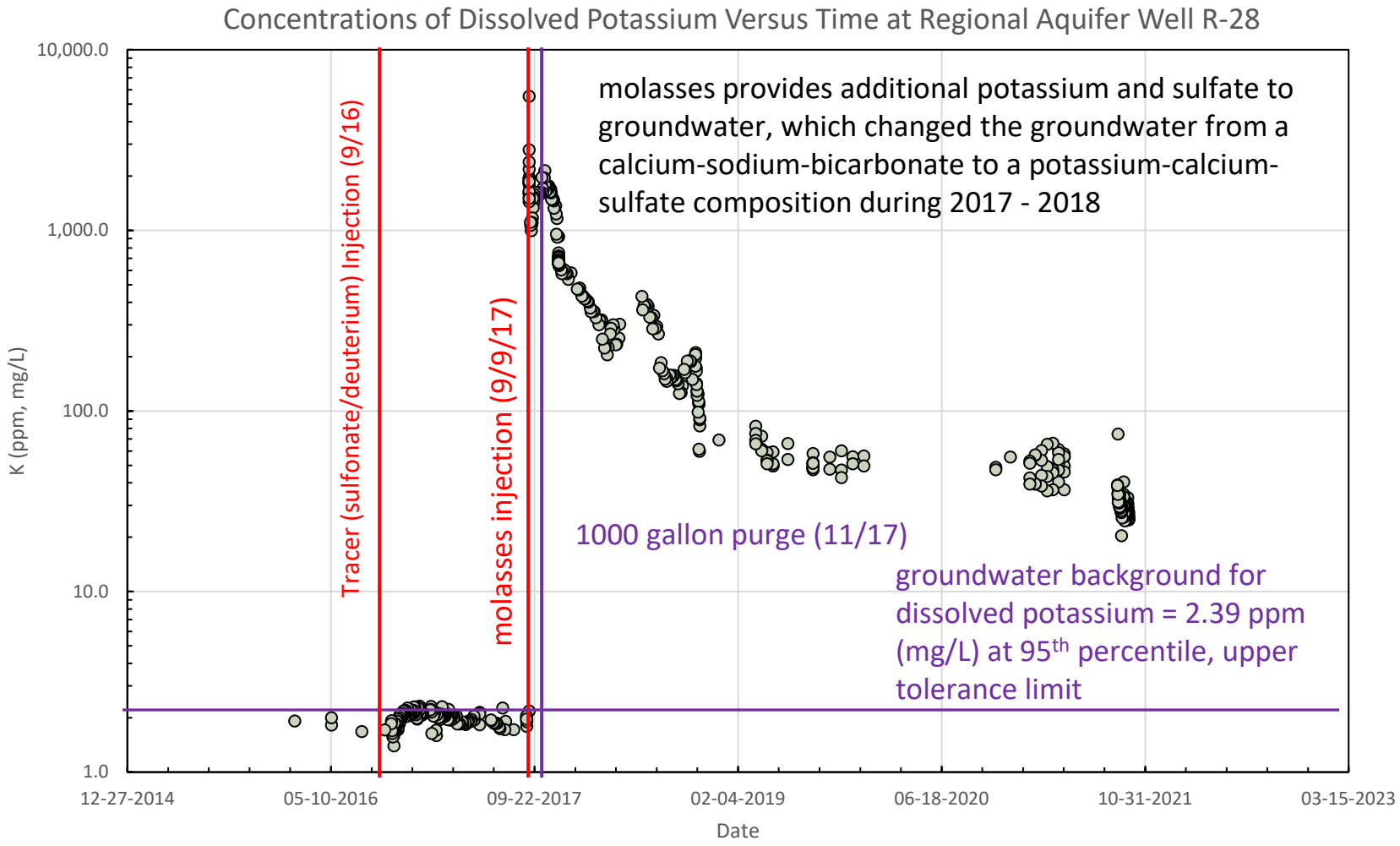
Concentrations of Dissolved Iron (Fe) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



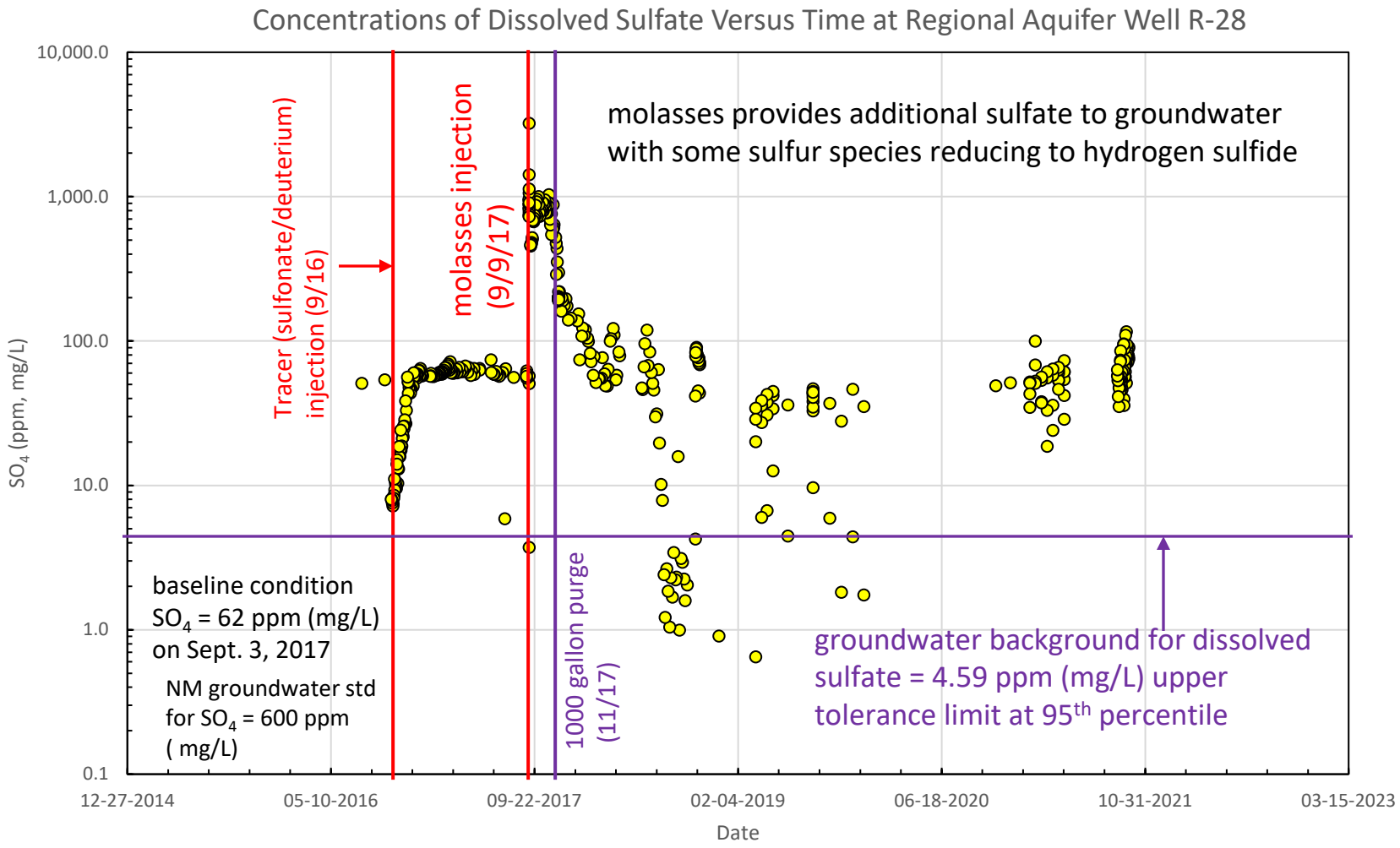
Concentrations of Dissolved Manganese (Mn) Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



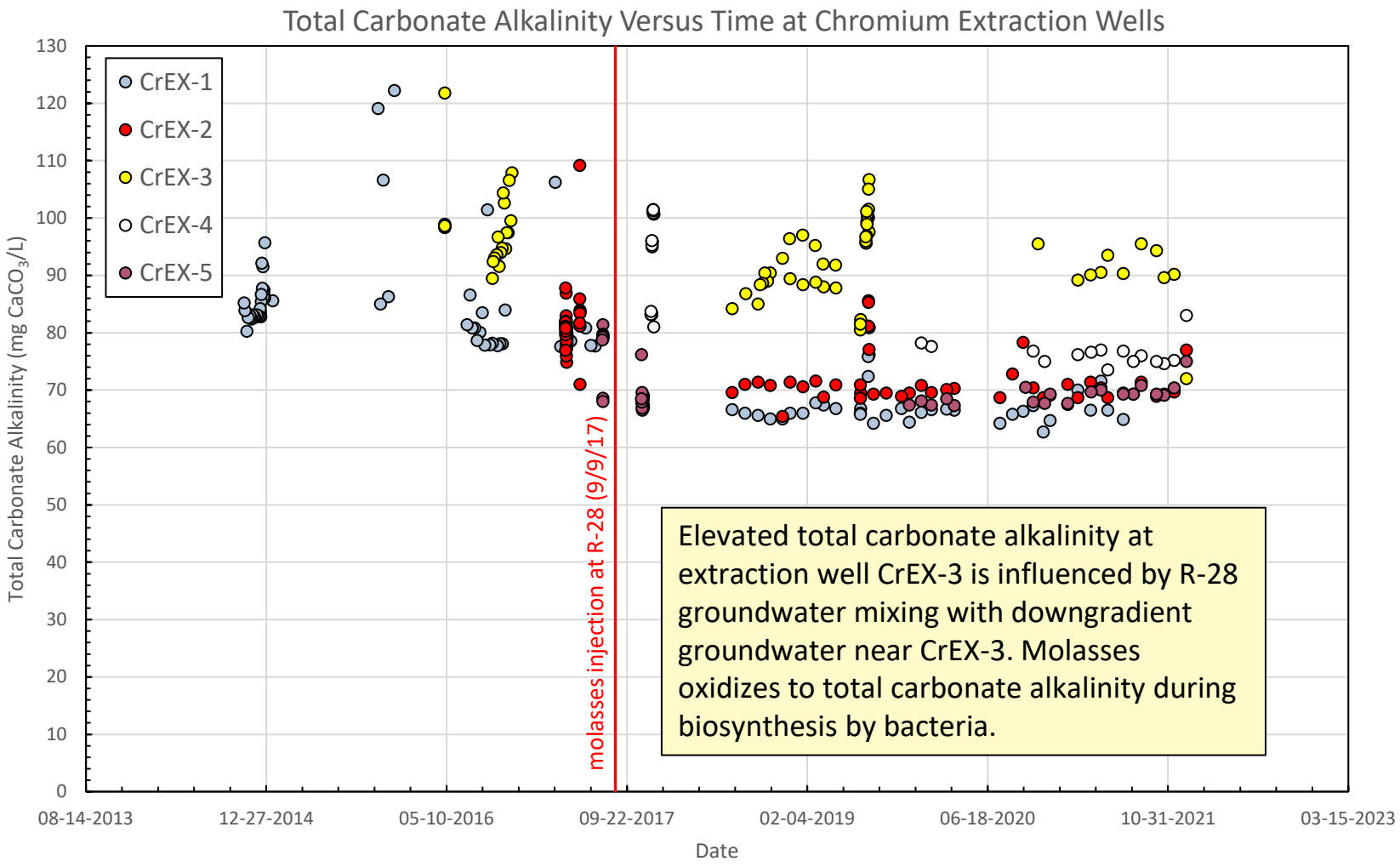
Concentrations of Dissolved Potassium Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



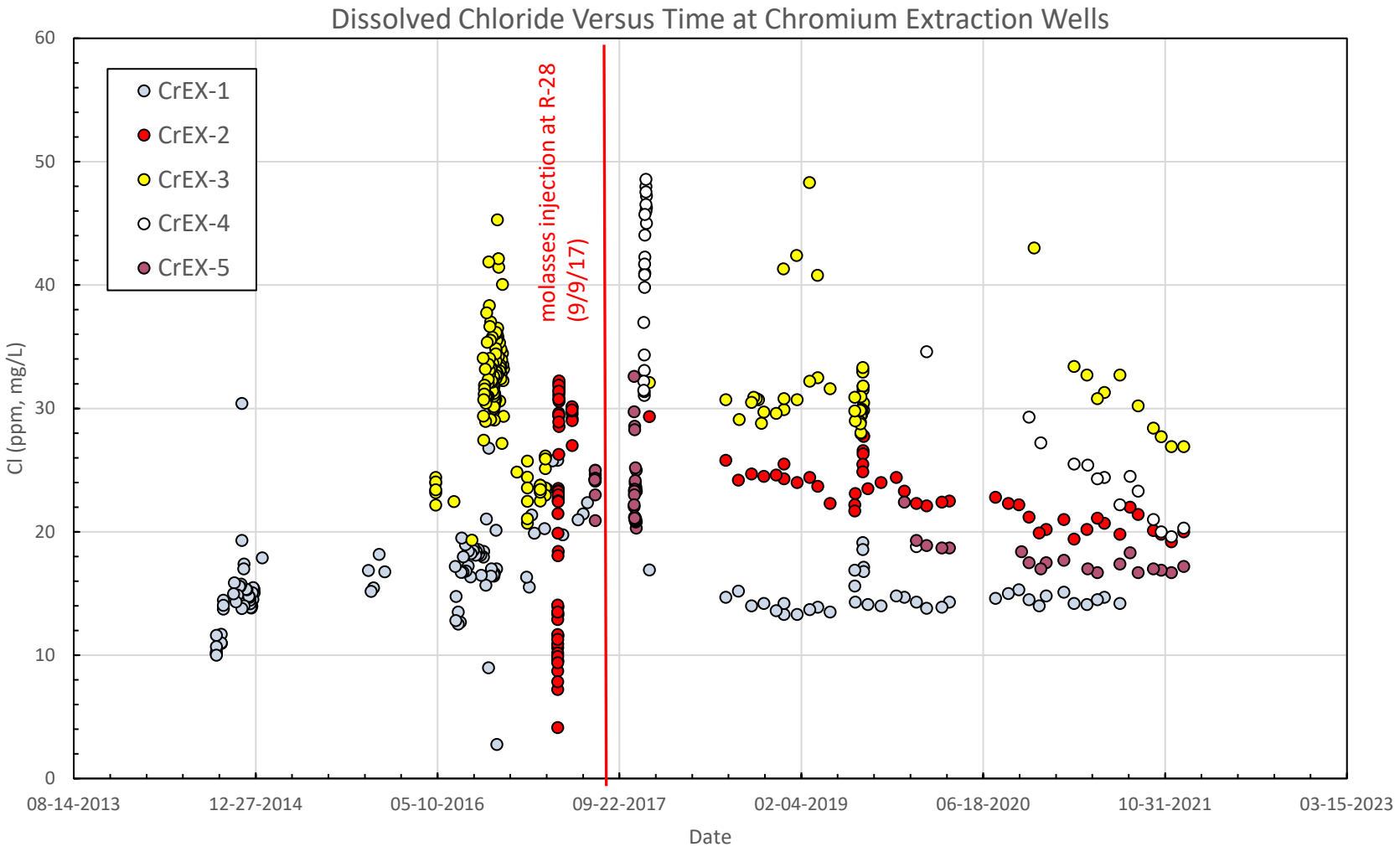
Concentrations of Dissolved Sulfate Versus Time at Regional Aquifer Well R-28 (source of data: DOE)



Total Carbonate Alkalinity Versus Times at Chromium Extraction Wells



Dissolved Chloride Versus Times at Chromium Extraction Wells



Dissolved Manganese Concentration Versus Time at Extraction Well CrEX-3