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CHROMIUM^{+6}
Deja Vu All Over Again

NEMC
August 15, 2011

Presentation Outline

1. History – Science and Society…
2. Chemistry of Chromium Sources and Forms
3. Analytical Issues
4. National Occurrence
5. Treatment process occurrence “anomalies”
6. Conclusions

Cr^{+6}: A 10 year+ Regulatory Timeline

Feb 1999 2.5 ug/L total Cr PHG (equivalent to 0.2 ug/L Cr^{+6})

Mar 1999 CDPH mandates Cr^{+6} monitoring

Mar 2000 “Erin Brockovich” released

May 2001 NTP study begins

Nov 2001 PHG rescinded based on expert panel

Apr 2003. Expert Panel findings rejected

May 2007 NTP declares Cr^{+6} a carcinogen by ingestion

Aug 2009, Draft PHG of 0.06 ug/L

Sep 2010 EPA releases new Cr^{+6} IRIS report

Dec 2010. EWG Report Released

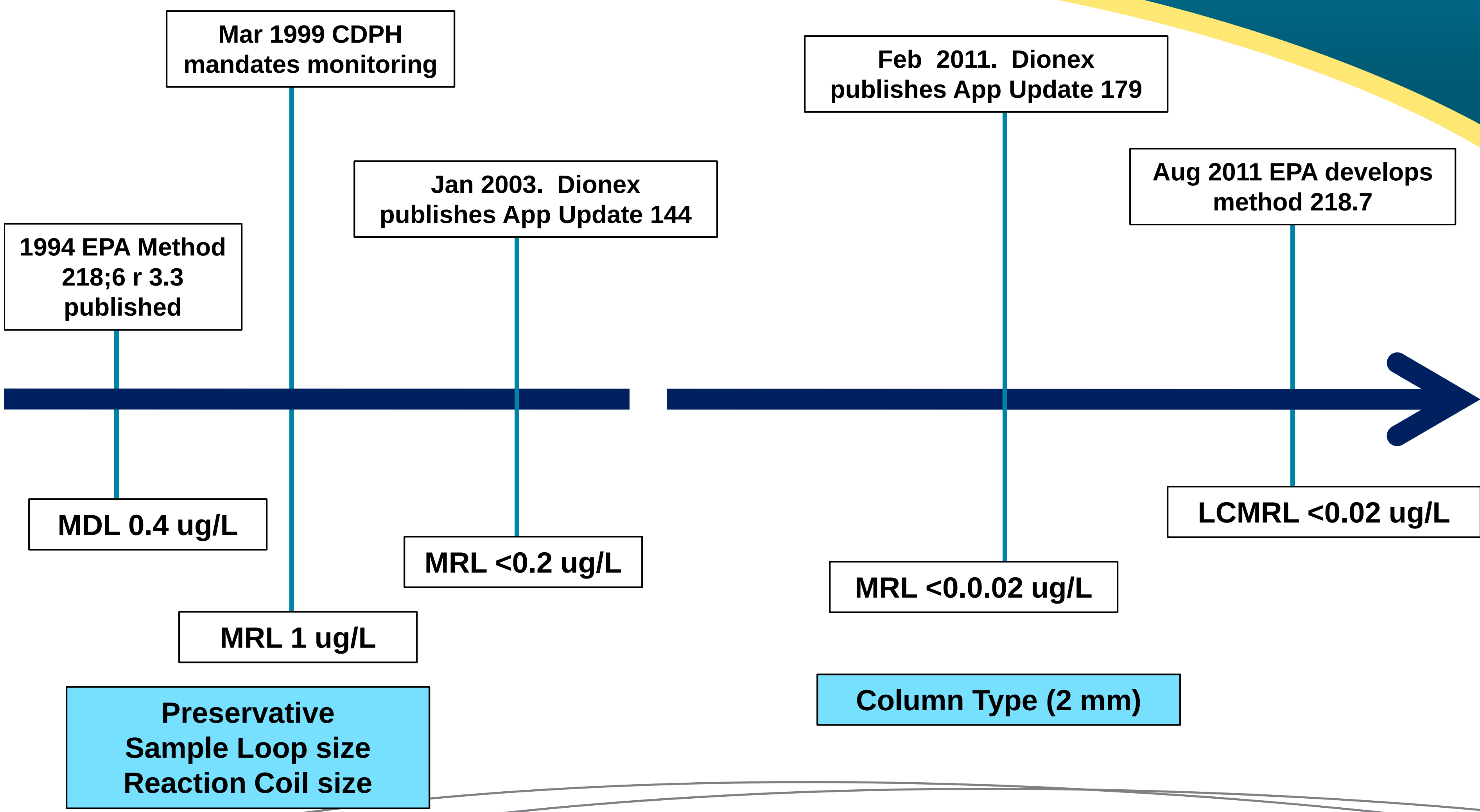
Mar 2011 EPA requests comments re including Cr^{+6} in UCMR3

Jul 2011 Final PHG of 0.020 ug/L

Aug 2011 EPA develops method 218.7

Chart concept courtesy of Nicole Blute (Arcadis)

Cr^{+6}: A 15 year+ Analytical Timeline



Chromium Exists as Several Chemical Species

Most common oxidation states: 0, +3, +6

0: Elemental Chromium (Cr)

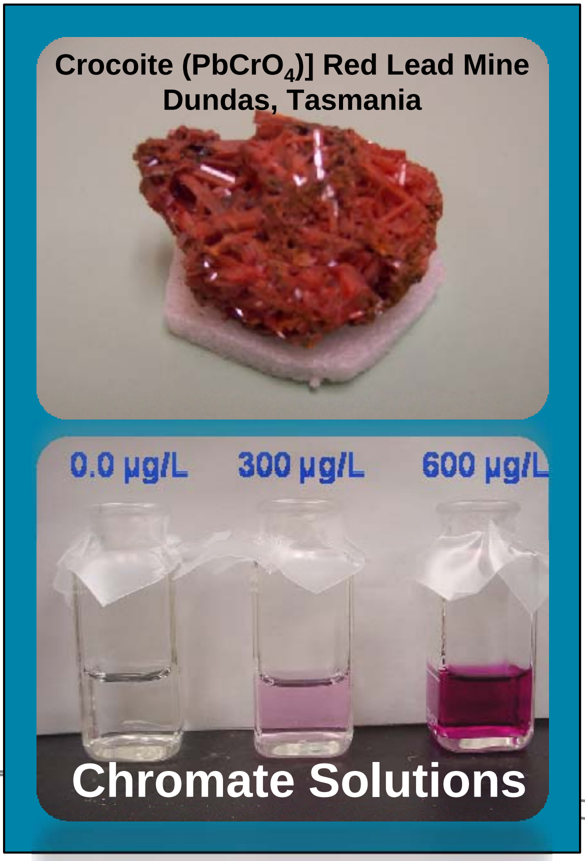
+3: Trivalent Chromium

Species: Cr^{+3}, Cr_2O_3

+6: Hexavalent Chromium

Species: CrO_4^{2-}, $Cr_2O_7^{-}$

Groundwaters – largely Cr^{+6}
Surface waters – more Cr^{+3}
Seidel (2004) AWWARF Study

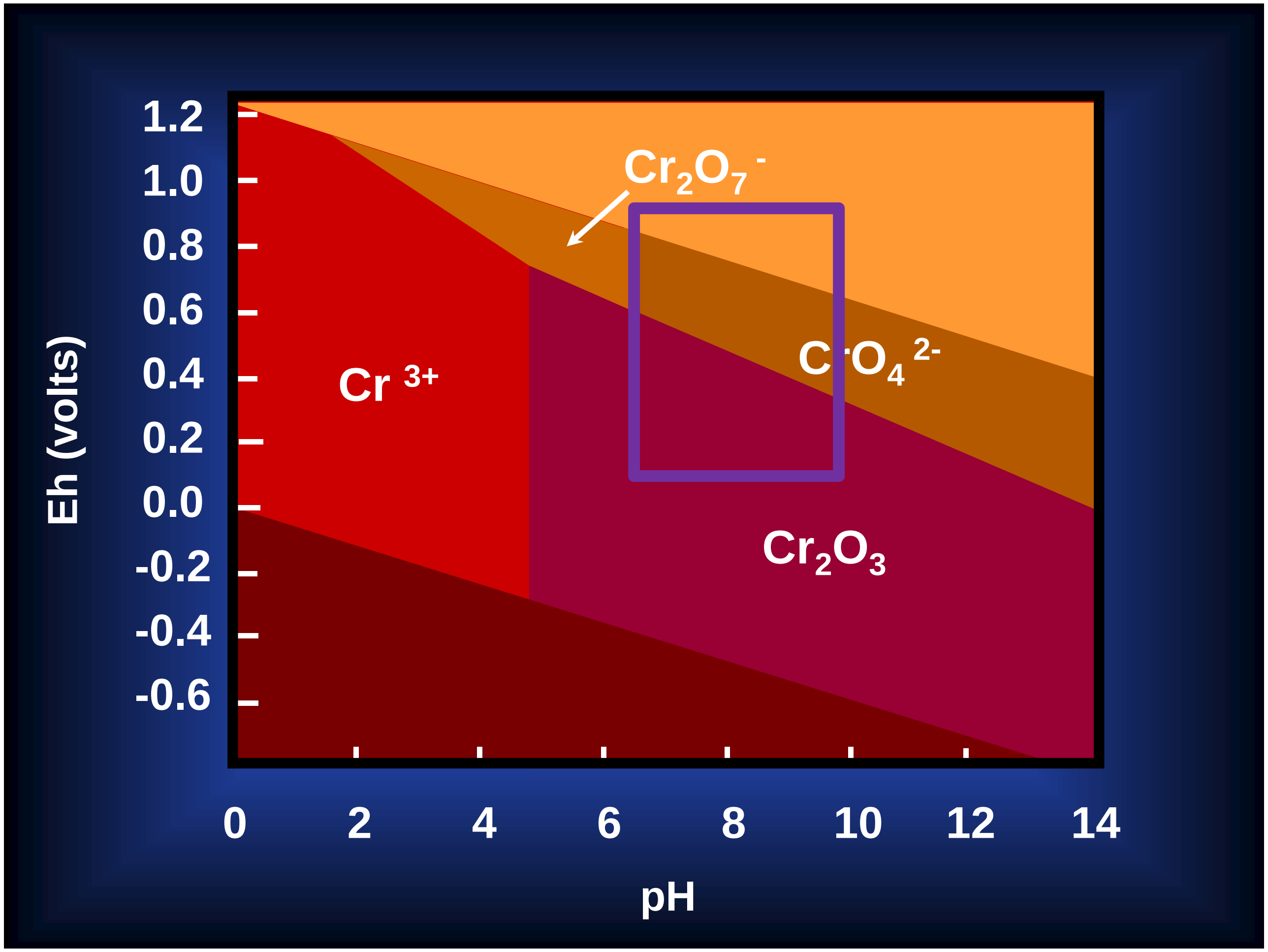


Forms of Chromium and Toxicity

- Trivalent (Cr^{+3})
  - Essential Nutrient
  - Converts to Hexavalent in the presence of oxidants

- Hexavalent (Cr^{+6})
  - Highly water soluble
  - Natural AND industrial sources
  - Carcinogenic by inhalation for sure; ingestion??
    - OSHA PEL = 5 ug/M^3
  - Converts to Trivalent in the stomach
  - Converts to Trivalent in the presence of Ferrous Iron

Chromium Speciation in Water (eH-pH Diagram for Chromium)

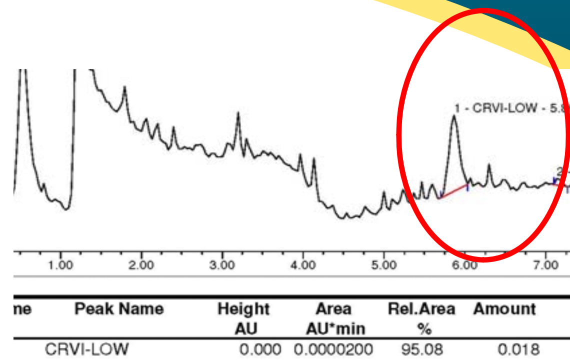


In most natural waters Cr^{+6} is the most soluble and stable form!

As will be shown, analytical data on occurrence supports this… thermodynamics works!

Analytical Issues for the Measurement of Hexavalent Chromium

- Ion Chromatography Methods for Cr^{+6} are EXTREMELY sensitive
  - Quantitative data at **0.020** ug/L



- Cr^{+6} is very stable in most waters
  - The holding time WAS 24 hours; now it is proposed as **2 weeks (EPA DRAFT method 218.7)**

- For Cr^{+6} lab blanks are not a big issue

- The challenge is to prevent oxidation of Cr^{+3}

Preservation Issues Depend on the eH-pH Diagram and Preventing Redox Reactions

- Bring the pH up
  - 218.6 said >9 (or 9.2-9.7)
  - **218.7 says >8**
  - 10 years worth of data in our lab supports the fact that you don't need to have the pH above 9…

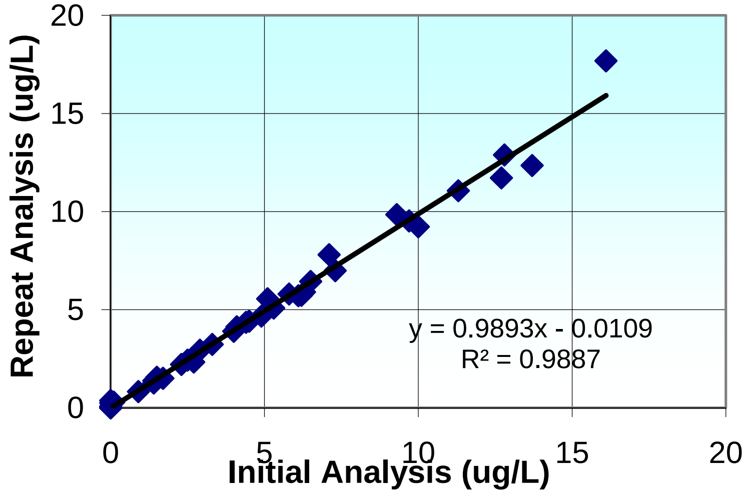
- Minimize the ability of free chlorine to oxidize Cr^{+3}
  - Add NH_4SO_4 to form chloramines
  - Work from EPA region 6 and EPA-Cincinnati demonstrates that this is effective
  - Without adding the ammonia, oxidation will occur
  - Also no impact from Fe (III) reduction

Buffering Options Have Varied Over the Years

- 218.6 (original) used strong NH_4SO_4/NH_4OH buffer
  - Impacted column capacity
  - Caused some signal suppression
- CDPH proposed a borate buffer
  - Did not address chlorine issues because CDPH measurements were source waters
- Newer methods (e.g. 218.7) use weaker buffers
  - Dilute NH_4SO_4/NH_4OH **(liquid)**
  - Sodium carbonate/bicarbonate + NH_4SO_4 **(solid)**

So: Analytical Issues for Cr^{+6}- Some Real, Some "Imagined"

- Holding Time?
  - 24 hours (original EPA 218.6), CAUCMR
  - 5 days (EPA DW Guidance)
  - 28 days (40CFR136)
  - 14 days (EPA 218.7)
- pH adjustment?
  - Greater than 9 (drinking water)
  - 9.2 to 9.7 (wastewater)
  - >8 (EPA 218.7)

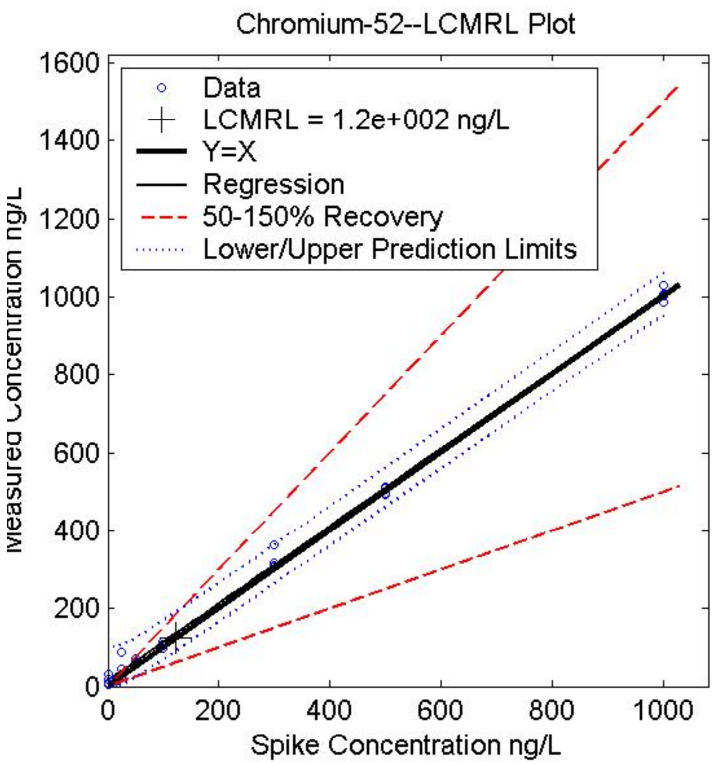


- Field Filtration in 218.6 (wastewater vs drinking water)
  - Cross Contamination. Is it even necessary?

In Draft Method 218.7 there Are Still Analytical "Issues" with Cost Implications

- How frequently do you need to prepare the preservative?
- Can you send liquid preservative to the field? (e,g, pre-preserve samples?)
- Do you need to filter samples before injection on the IC?
- Do you need to chill samples during transport?

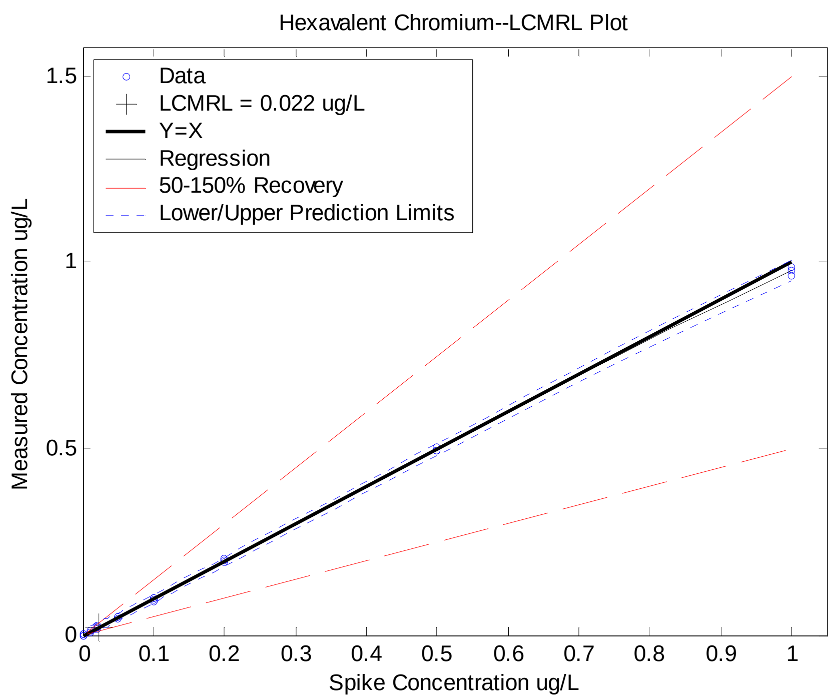
Comparing LCMRLs for Cr^{+6} and Total Chromium. Cr^{+6} method is 5-10X more sensitive



MWH Total Chromium LCMRL =

120 ng/L

(DI water with digestion)



EPA 218.7 Chromium-6 LCMRL =

22 ng/L

Total Chromium Measurements Are More Problematic

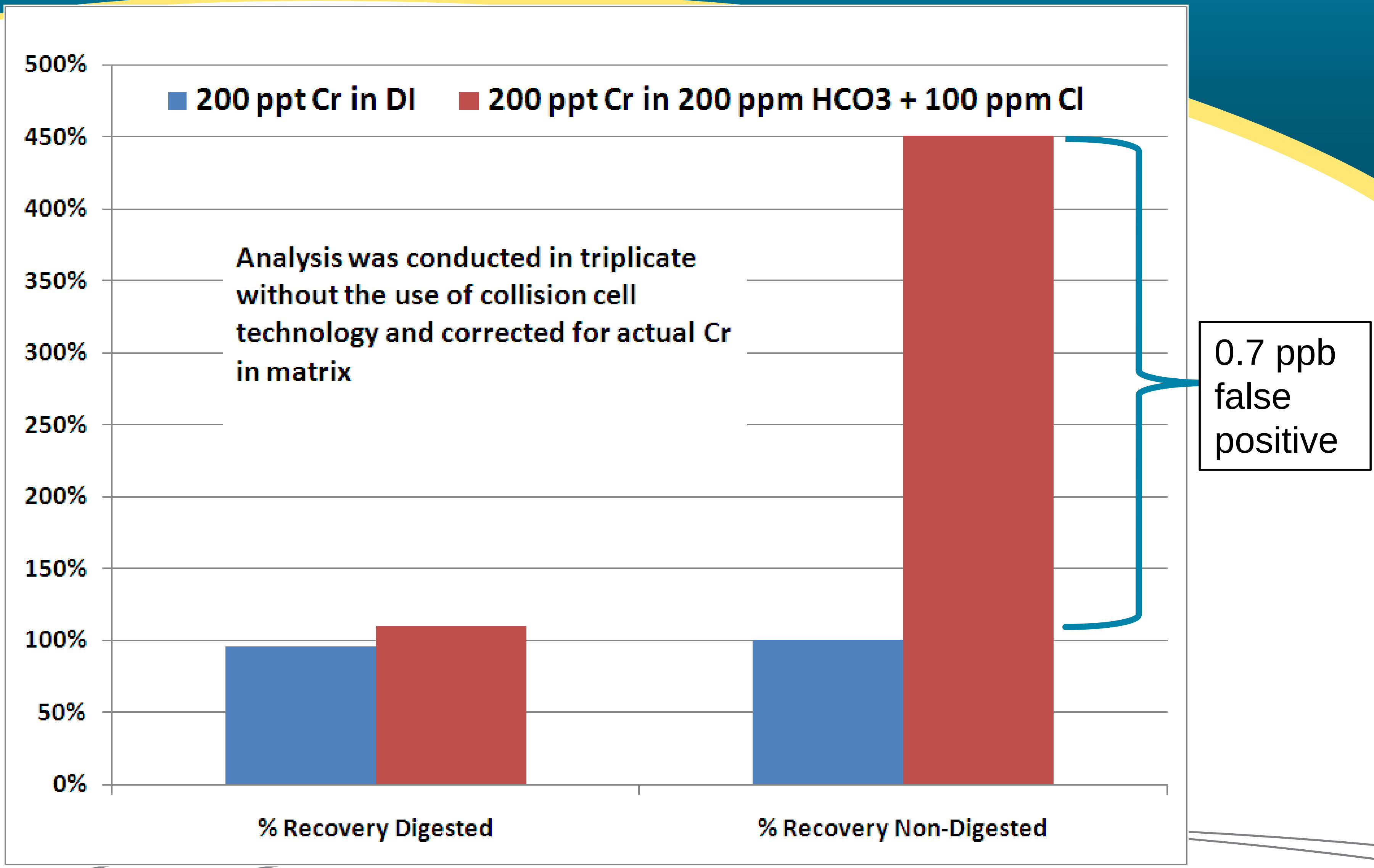
- Chromium has 2 major stable isotopes at mass 52 (83.8%) and mass 53 (9.5%)

- Traditional ICPMS is prone to interferences from ArC (mass 52) and ClO (mass 53)

- For UCMR3 EPA recommends digestion (regardless of turbidity) to minimize the ArC interference

- Collision cell technology is not yet permitted for drinking waters

Does Digestion Solve the Carbon Interference Problem?

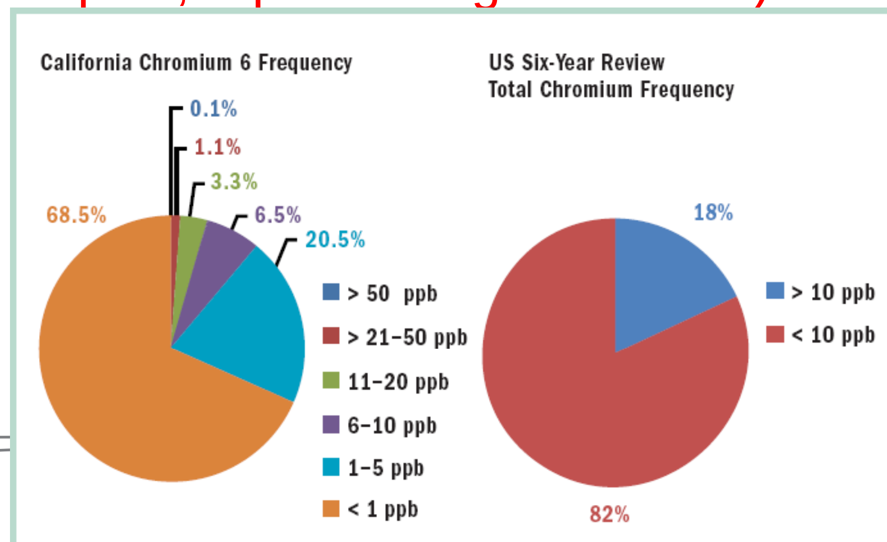


Occurrence Data Impact Will Depend to a Large Extent on Toxicity Decisions

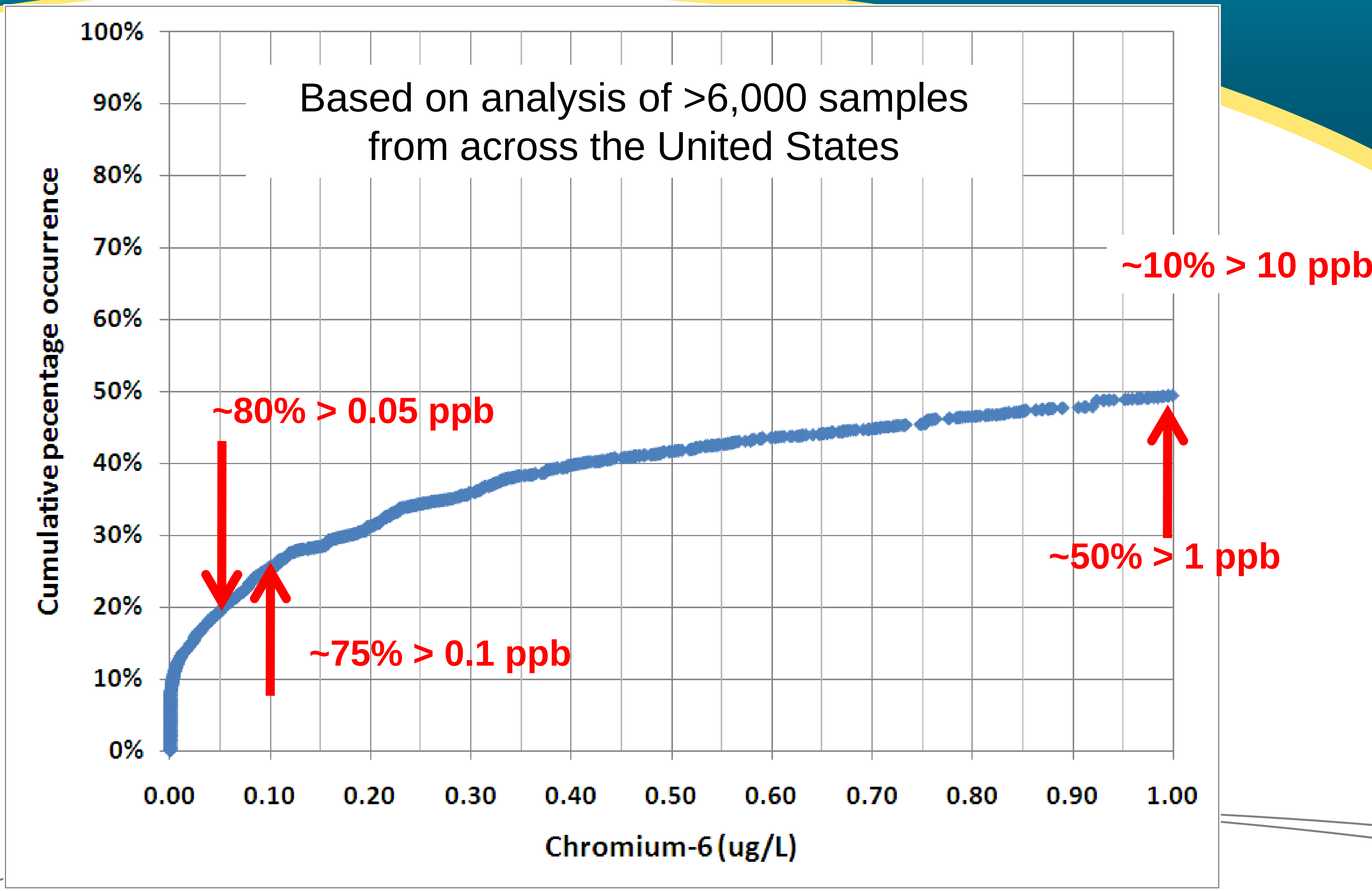
- Some existing public data gives a sense of what's present, but not the whole picture.
- What if you start looking at lower levels?
- What about Cr^{+6} vs Cr^{+3} occurrence?
- What happens in treatment plants?

Chromium^{+6} Occurrence

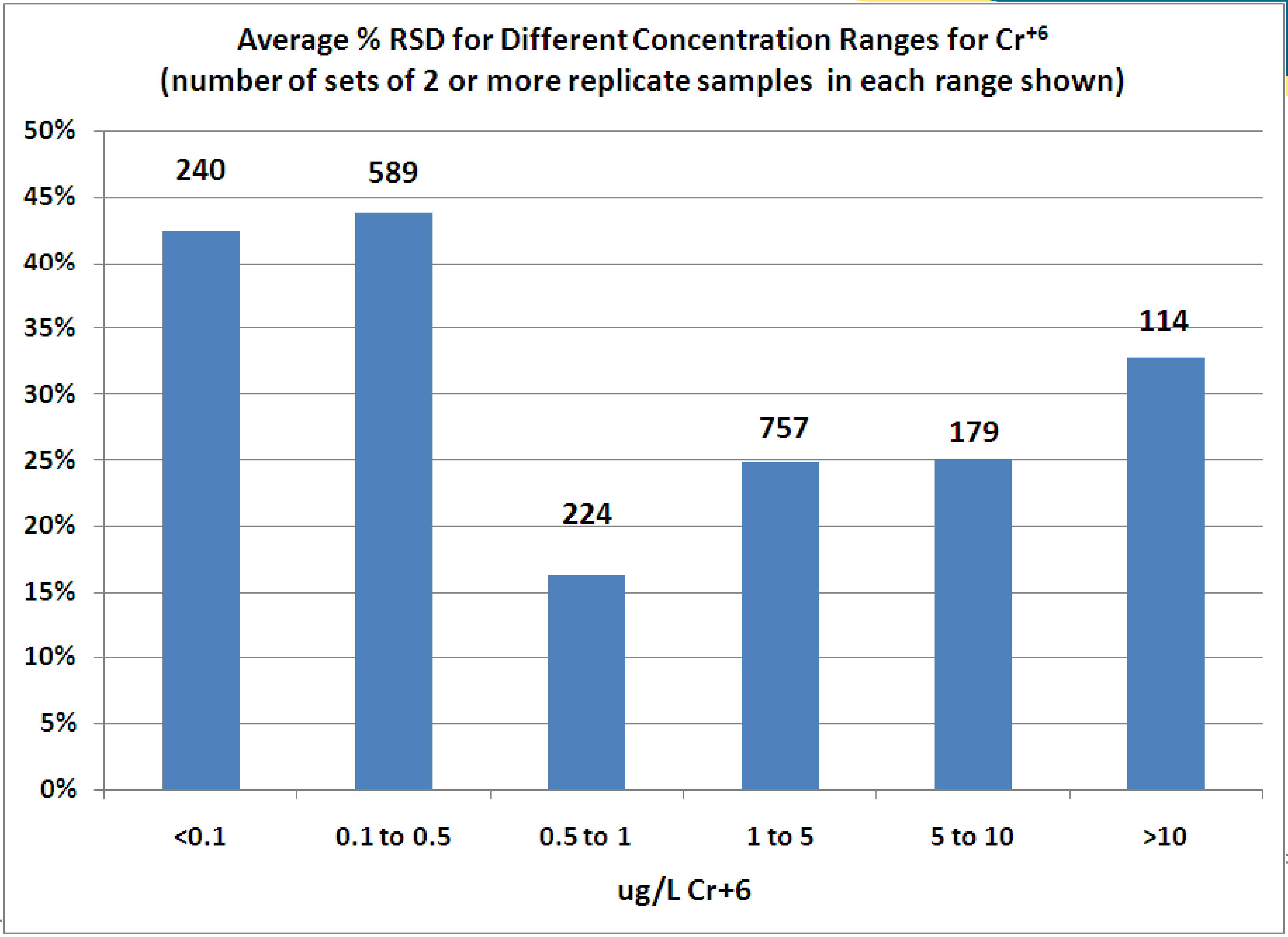
- EPA National Occurrence (6-year review data)
  - 18% of sources >10 ppb (total chromium-not $^{+6}$ only)
- California (CA-UCMR data for Cr^{+6})
  - 11% of sources >10 ppb (hexavalent)
  - 33% of sources >1 ppb
- MWH (Cr^{+6}) (1500 non California samples, representing 2011 data)
  - 1% >10 ppb
  - 20% >1 ppb
  - 50% >0.1 ppb
  - 70% >0.05 ppb



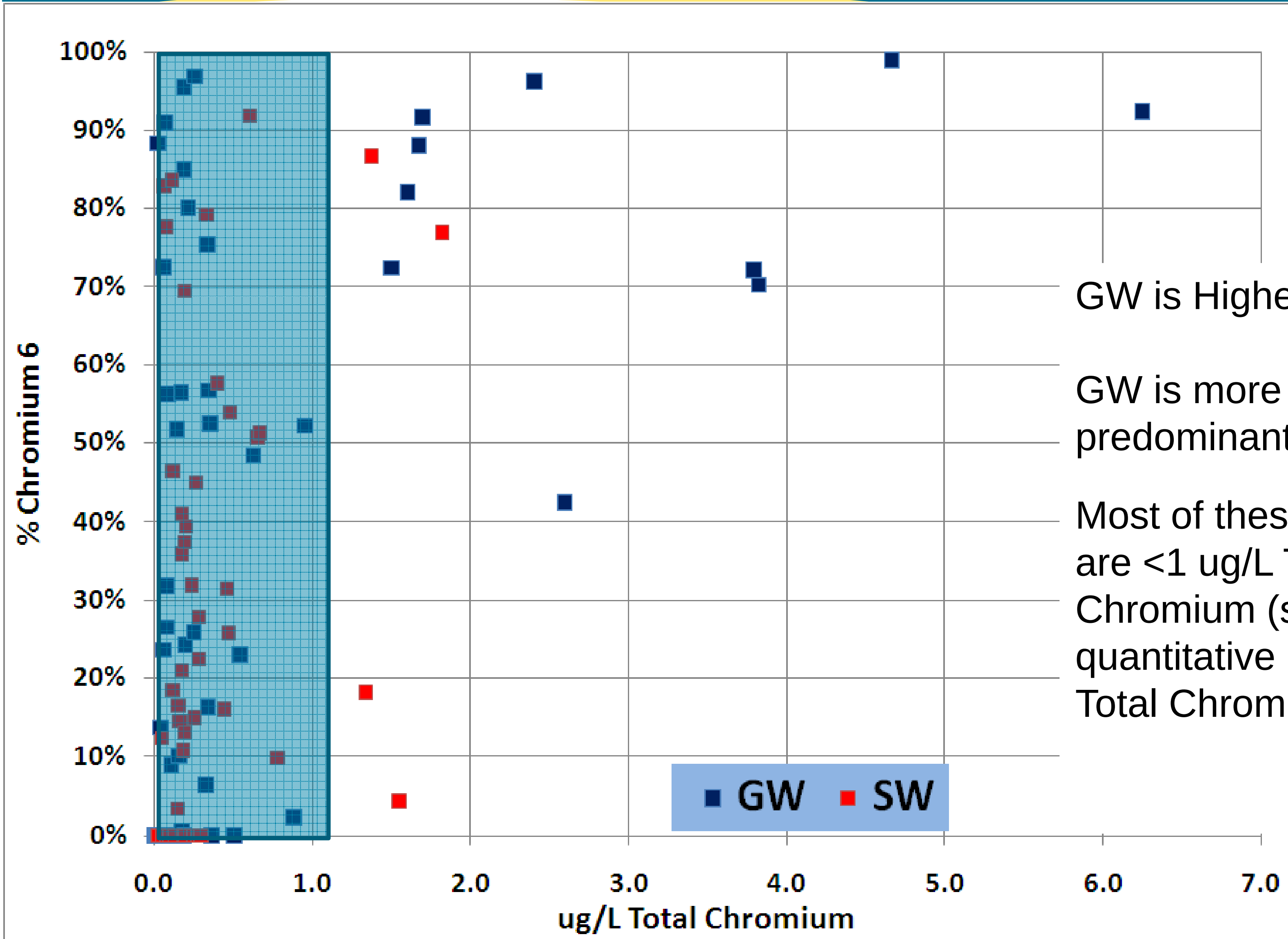
Cr^{+6} Occurrence – the Lower We Look the More We Will Find….



How Much Does Cr^{+6} Vary Over Time? Answer: Not Very Much



Paired Distribution System Samples (Cr-T and Cr^{+6}) From GW or SW Show Trends



GW is Higher Than SW

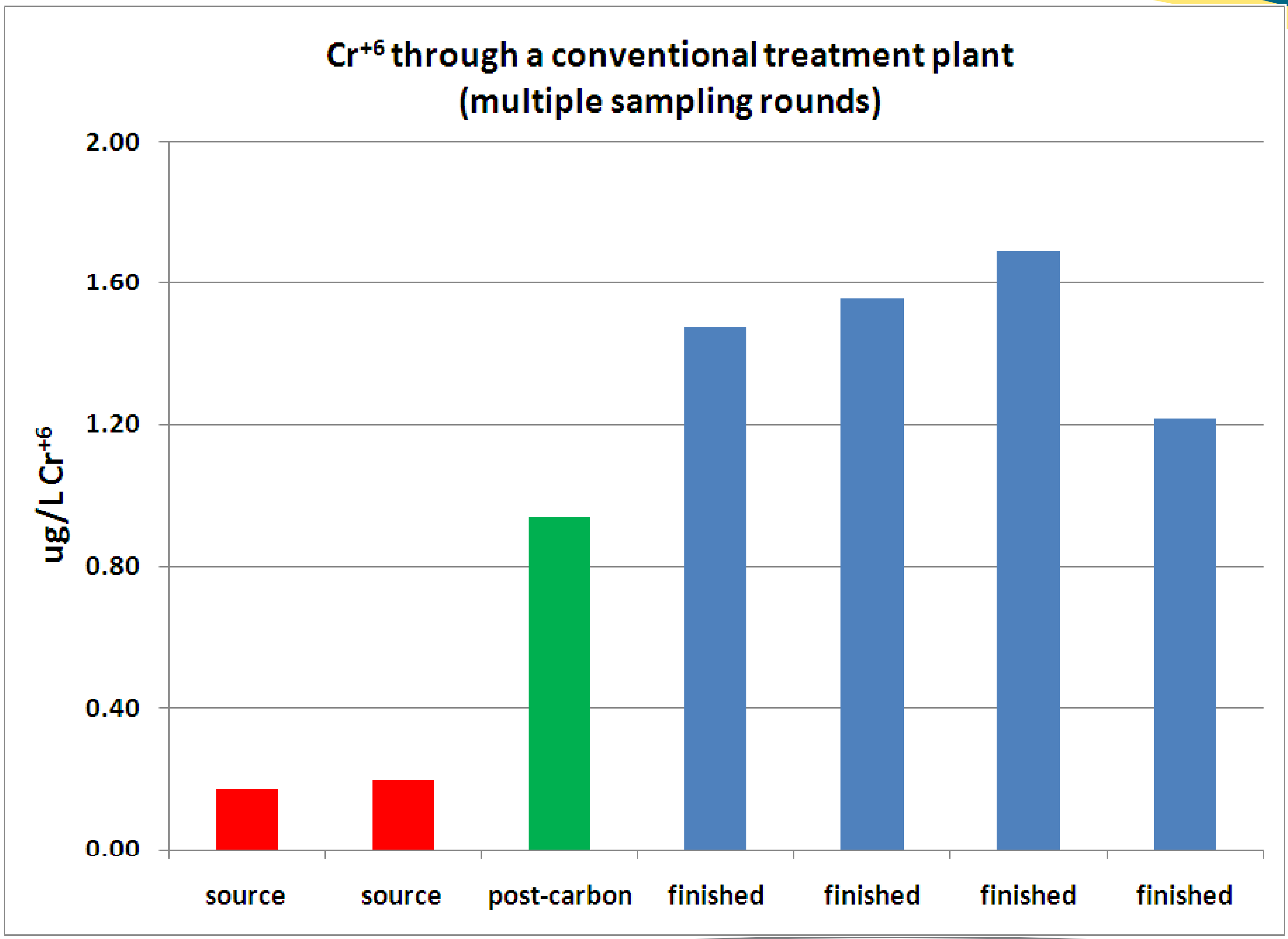
GW is more likely to be predominantly Cr^{+6}

Most of these samples are <1 ug/L Total Chromium (semi-quantitative range for Total Chromium)

Potential for Chromium Cross Contamination (or analytical errors)?

- Stainless Steel (10%+ Chromium)
  - Could leach Cr^{+3} under acidic conditions
- Buffer Chemicals used for pH adjustment
  - NaOH has traces of Cr^{+6}
  - KCO_3 has traces of Cr^{+6}
- ICP/MS Carbon Correction (Eaton, 2001)
  - ArC in ICPMS has same mass as Cr (52)
- Treatment process adding Cr^{+6}
  - Source water   0.15 ppb
  - Treated after coagulant – 1.5 ppb

A Few Interesting Tidbits of Cr^{+6} Occurrence Through a Conventional Treatment System



Note that this is UNUSUAL – we **<u>have not seen</u>** the increase in all plants we have studied.

Total Chromium results mimic the Cr^{+6}, so this is likely Cr being added from treatment chemicals

What About RO Treatment?

- In general RO is very effective at removing chromium…..

- But again, we have on occasion seen cases where Cr^{+6} is detected in RO permeate at levels in excess of 0.2 ug/L.

- This seems more likely to be leaching from pipes than actual RO breakthrough, but the jury is still out.

Conclusions- Analytical Methods Assessment

- Hexavalent chromium by ion chromatography (e.g. 218.6 or 218.7) is a rugged and sensitive analytical method.

- Total chromium by ICPMS using drinking water approved methods is rugged down to 0.2 ppb, IF samples are digested. Otherwise you may get positive bias (up to low ppb levels).

- Collision cell technology should also address the bias issues, but is not approved for DW yet.

Conclusions – Precautions and Occurrence

- The analytical issues relate more to sample collection than analysis per se.

- There is ample evidence that Cr^{+6} is widespread at low levels. Health effects and treatment costs will trump occurrence as drivers.

Any Questions?

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