



Hexavalent Chromium and Total Chromium in Natural Waters – Can We Ensure Accurate Measurements at sub-ppb Levels?

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Presentation Outline



1. Existing Occurrence Data – What does it tell us?

2. Can You Trust These Numbers?

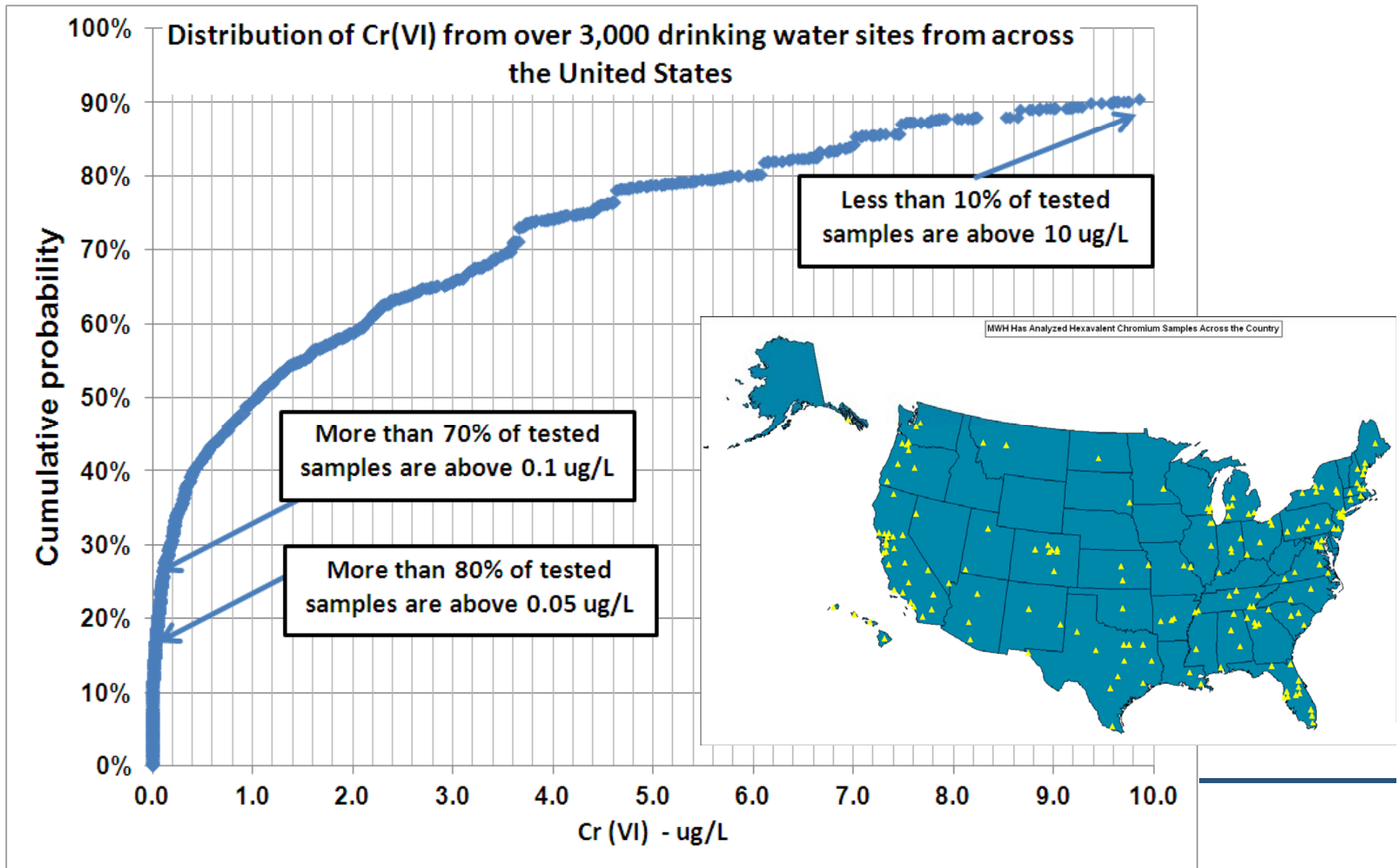
– Approaches to Analysis of Chromium (VI) and Total Chromium

Cr (VI): 218.6 vs 218.7

Total Chromium: collision cell, digestion, carbon correction

3. Conclusions

We Have a Very Large Internal DW Database – That Goes Down to <math><0.05\text{ ppb}</math>



2011 Cr (VI) Drinking Water Sample Summary (6500 samples across the U.S.)



Frequency of Occurrence	Cr (VI) Conc (ug/L)
75%	0.04
50%	0.24
25%	2.15
10%	6.89

The lower we look the more we see

Our Data Can Actually be Put Into Three Bins



Total Set (~3000 sites) (many sampled more than once)

Total Non-California Set (~1500 sites)

- **Has some bias towards PWS with known Cr(VI) issues (e.g. Hawaii)**

A smaller set (~100 sites) of distribution system samples from across the country that have been measured for a variety of constituents for 6 years, with Cr (VI) added to the target list in 2011. This set should have no inherent Cr (VI) bias, but does not reflect populations and also has more surface water sites than groundwater.

So Now Lets Slice and Dice The Cr(VI) Data a Bit More



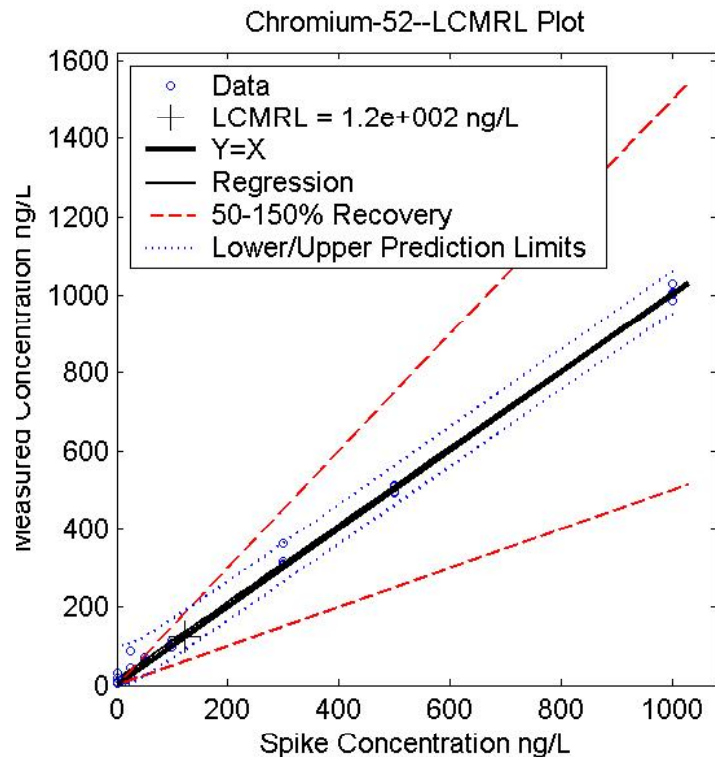
Concentration Range	CA-UCMR data	AWWARF 2004 survey (Seidel)	American Water 2011 (Corson)	EEA Total sample sites	EEA Non California sites	EEA "National" Sample Sites
Count	~7000	341	1100	~3000	~1500	100
>10 ppb	5%	<1%	3%	10%	1%	<1%
>1 ppb	33%	~20%	24%	50%	20%	10%
>0.1 ppb	NA	NA**		75%	50%	35%
>0.05 ppb	NA	NA	62%***	80%	70%	57%
>0.02 ppb	NA	NA		90%	80%	75%

**AWWARF survey had an MDL of 0.2 ppb

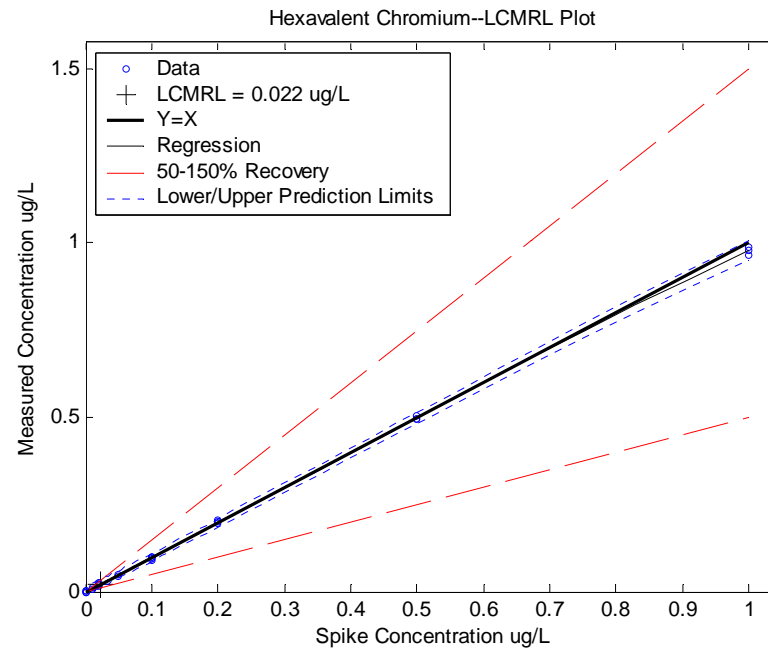
*** American Water was actually 0.06 ppb MRL

It is likely that a minimum of 10-20% of PWS sites will have >1 ppb Cr (VI) and >60% of PWS sites will be >0.05 ppb Cr (VI).

Comparing LCMRLs for Cr (VI) and Total Chromium.



**Our Total Chromium LCMRL =
120 ng/L
(DI water with HNO₃ digestion)**



**EPA 218.7 Chromium (VI) LCMRL =
22 ng/L**

What About Total Chromium Data?



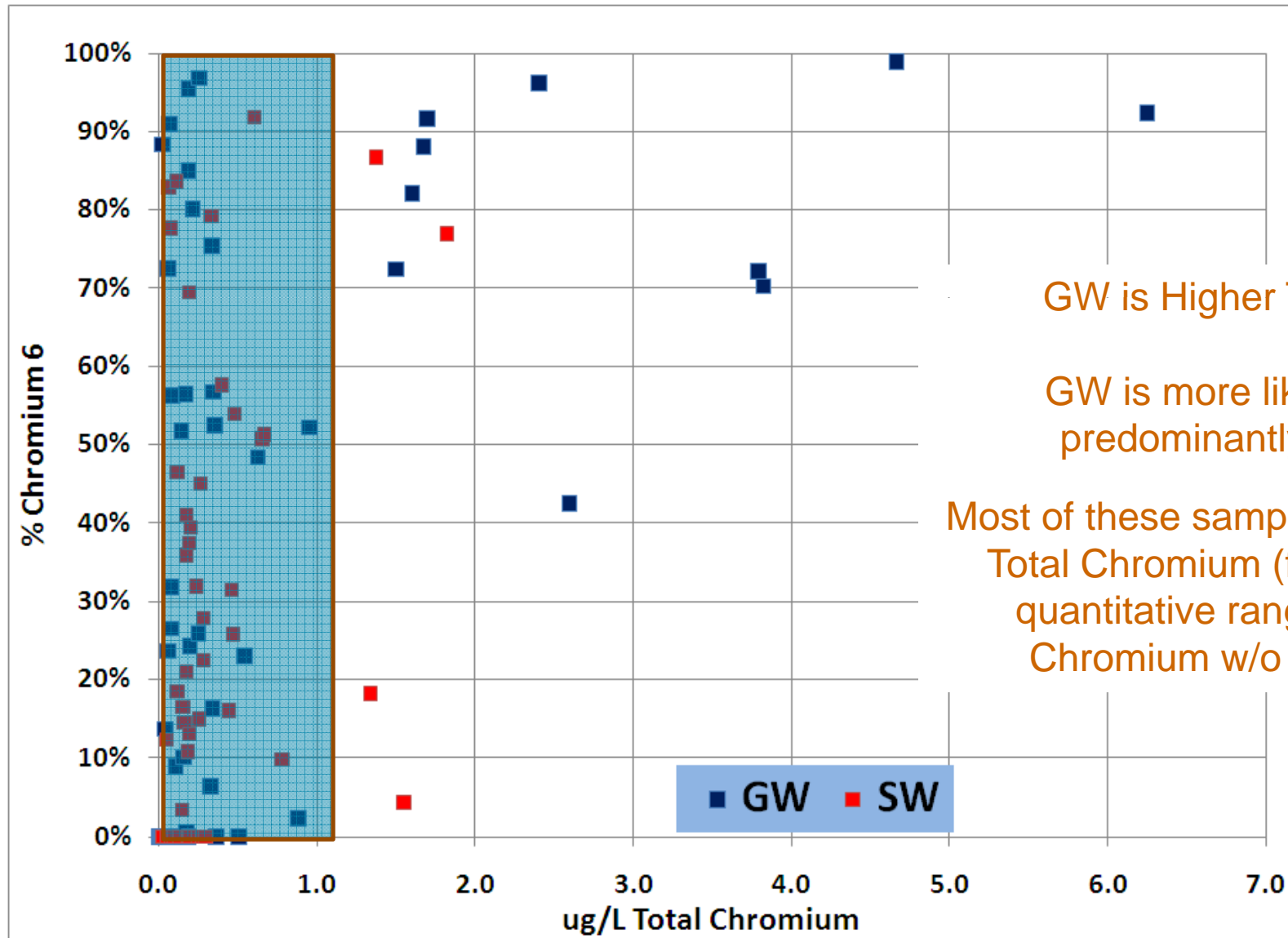
Historically most drinking water compliance measurements for total chromium have had much higher MRLs

- With MCLs of 50 (some states) to 100 ppb, there has been no incentive to measure at low levels
- Most regulatory data has MRLs of 10 ppb so there is not as much data with low MRLs (e.g. 1 ppb or less)

EPA's UCMR3 monitoring will require measurements at much lower levels (0.2 ppb MRL, with MDL <0.07 ppb)

HOW DO WE ENSURE ACCURATE MEASUREMENTS?

Paired Distribution System Samples (Cr-T and Cr(VI)) From GW or SW Show Trends



GW is Higher Than SW

GW is more likely to be predominantly Cr (VI)

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

What About The Potential for Chromium Cross Contamination?



Stainless Steel (10%+ Chromium)

- Could leach Cr (III) under acidic conditions and then be oxidized by chlorine, but no real evidence this is a major issue

Buffer Chemicals used for pH adjustment

- NaOH has traces of Cr (VI)
- K_2CO_3 has traces of Cr (VI)

Treatment process chemicals

- Louisville KY has demonstrated that they were generating Cr (VI) in their treatment train and controlled it via changing disinfection point.

Analytical Issues for Cr-T and Cr-VI



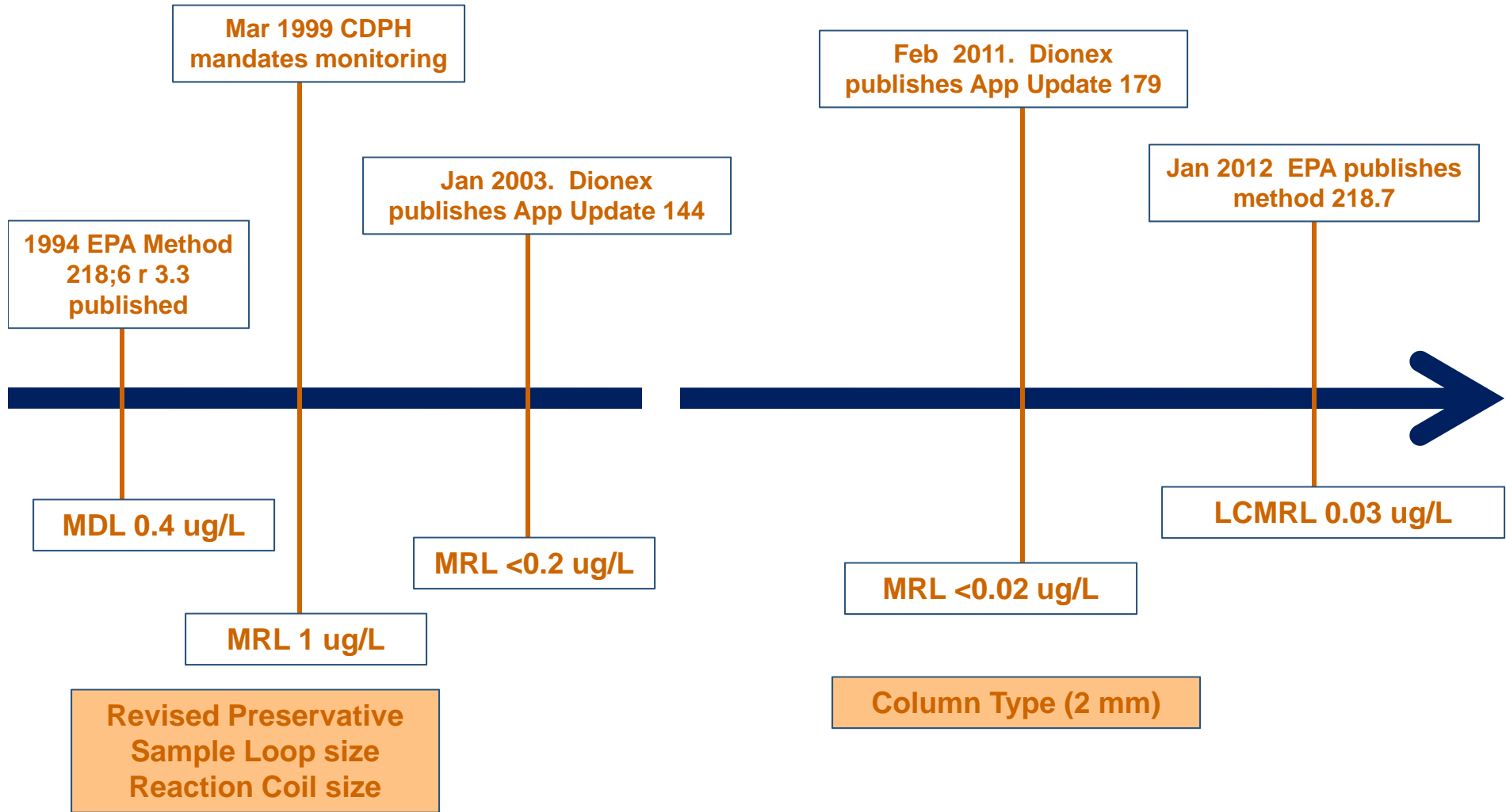
Hexavalent chromium

Evolution from 218.6 to 218.7

Total Chromium

Different approaches to addressing interferences

Cr (VI): A 15 year+ Analytical Timeline



Analytical Issues for the Measurement of Hexavalent Chromium



Ion Chromatography Methods for Cr (VI) are **EXTREMELY** sensitive

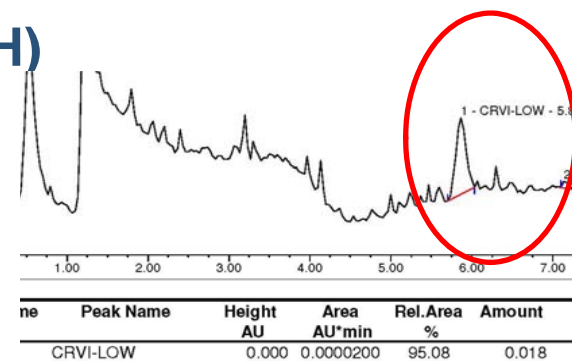
- Quantitative data at 0.020 ug/L

Cr(VI) is very stable in most waters

- The holding time **WAS** 24 hours; EPA 218.7 is now 2 weeks (provided you check for free chlorine and pH)

For Cr(VI) lab blanks are not a big issue

The challenge is to prevent oxidation of Cr (III)



Preservation Depends 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 (you don't need to be as high as 9)

Minimize the ability of free chlorine to oxidize Cr (III)

- Add NH_4SO_4 to form chloramines
- Without adding the ammonia, oxidation WILL occur and you can end up with false positives.

Buffering Options Have Varied Over the Years



218.6 (original) used strong $\text{NH}_4\text{SO}_4/\text{NH}_4\text{OH}$ buffer

- Impacted column capacity
- Caused some signal suppression

CaDPH proposed a borate buffer

- Did not address chlorine issues because CaDPH measurements were source waters
- McNeill (2012) showed that borate is NOT reliable with chlorine present.

Newer method (e.g. 218.7) uses weaker buffers

- Dilute $\text{NH}_4\text{SO}_4/\text{NH}_4\text{OH}$ (liquid)
- Sodium carbonate/bicarbonate + NH_4SO_4 (solid)

So: Analytical Issues for Cr⁺⁶- Some Real, Some “Imagined”



Very Short Holding Time?- **imagined**

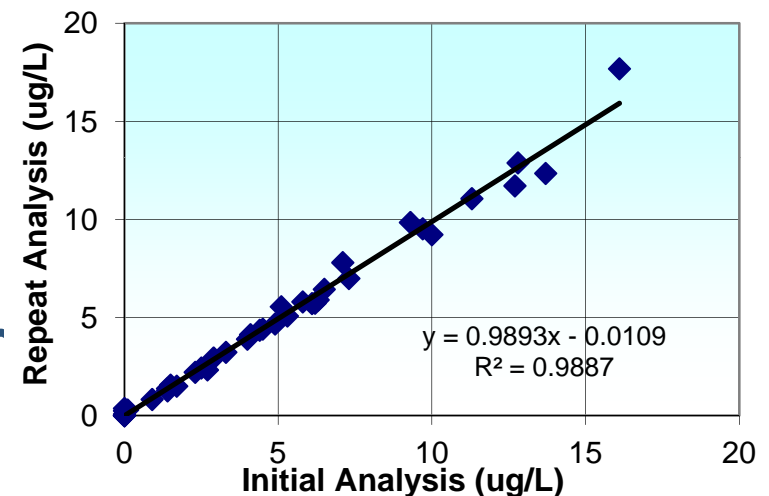
- 24 hours (original EPA 218.6), CAUCMR
- 5 days (EPA DW Guidance)
- 28 days (40CFR136)
- 14 days (EPA 218.7)

pH adjustment? – **partially real**

- Greater than 9 (drinking water)
- 9.2 to 9.7 (wastewater)
- >8 (EPA 218.7)

Field Filtration in 218.6 (wastewater vs drinking water)

- Potential Cross Contamination. Is it even necessary?
- Not required in 218.7



In Method 218.7 ALL the Knotty Analytical Issues Have Been Resolved



How frequently do you need to prepare the preservative?

Only once every 30 days

Can you send liquid pre-preserved samples to the field?

Yes, and must be used within 30 days

Do you need to prefilter samples before analysis

No longer necessary

Do samples need to be chilled during shipment?

No longer necessary

However, We Still Don't Get Off Completely Free...



Must check for free chlorine before analysis

- **<0.1 ppm**

Must check pH before analysis

- **>8**

Note that method says “upon receipt”, but EPA (in correspondence) has defined that as “before analysis”

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)

In UCMR3, EPA will require digestion w HNO_3 (regardless of turbidity) to minimize ArC interference

Collision cell technology is not yet permitted for drinking waters (and is also not fool proof)

Assessing Total Chromium Data Accuracy



Siedel AWWARF Study (2004)

Data preceded true understanding of challenges at these levels but did paired Cr (VI) and total Cr

Eaton et al (2011)

Showed significant false positives with sub ppb level measurements with ICPMS, even with carbon correction

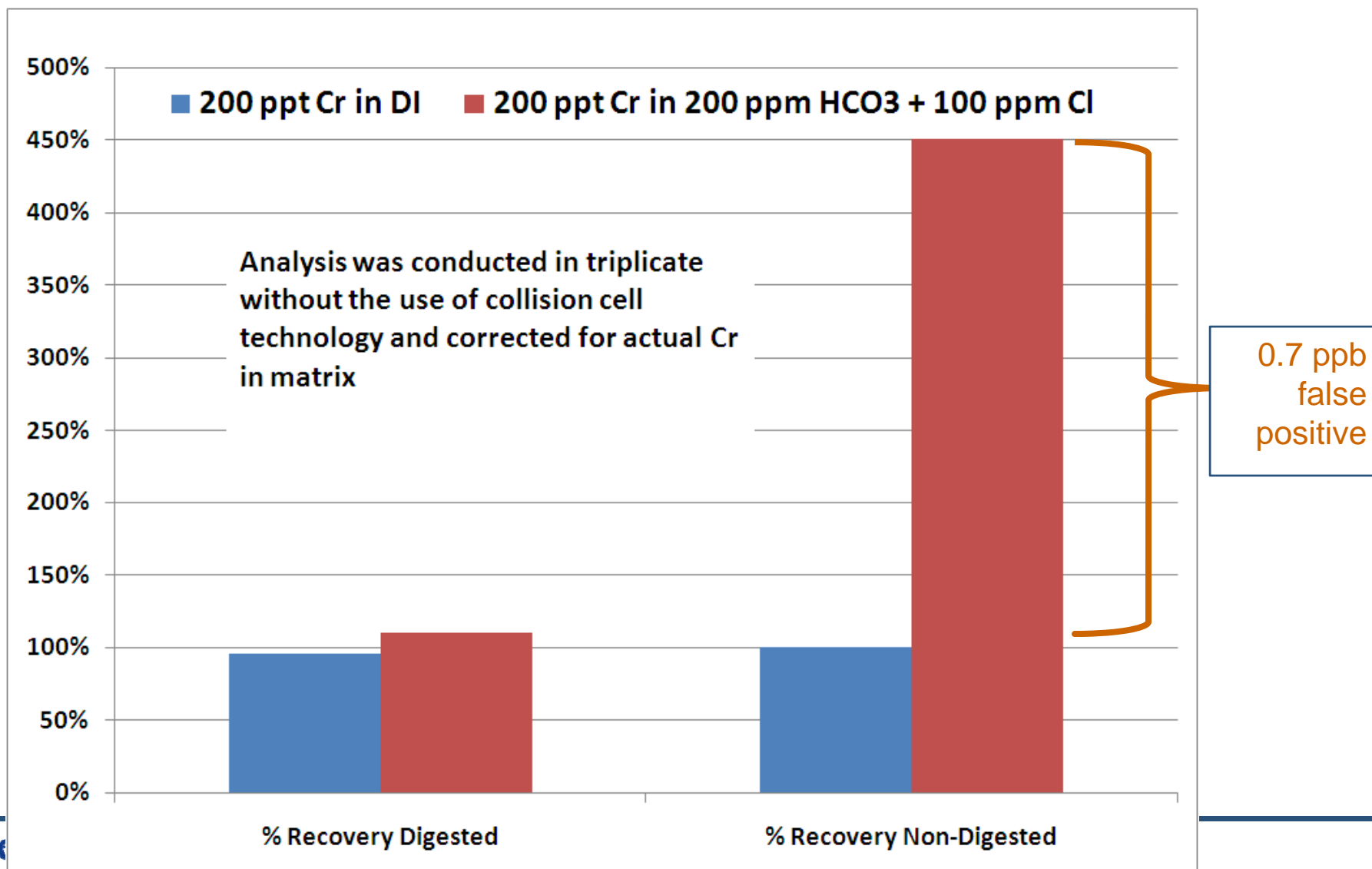
McNeill et al (2012) WaterRF

Studies evaluating analytical issues for both total chromium and chromium (VI) measurements at low levels

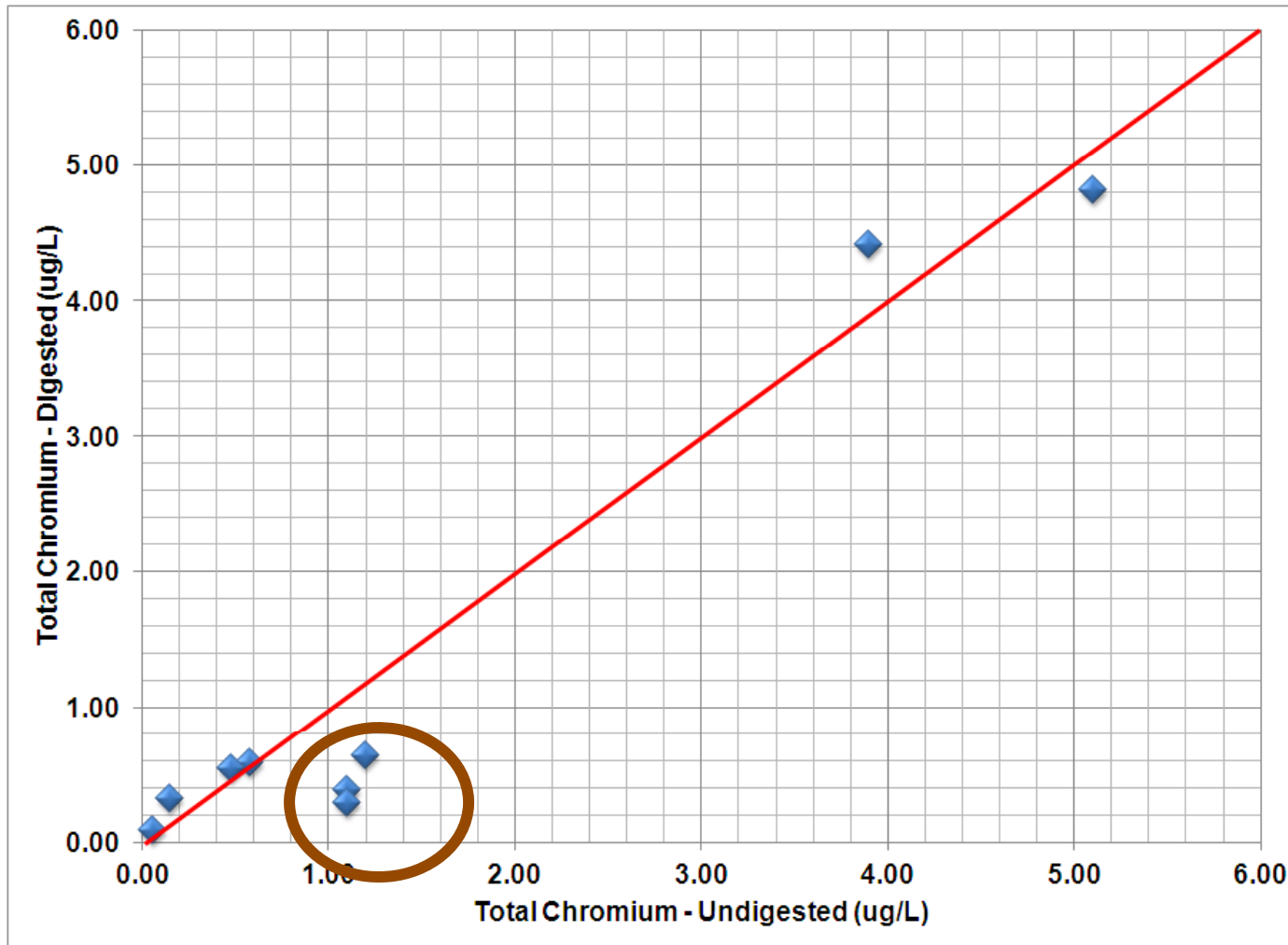
Beyene et al (2012)

Compared collision cell and digestion on various types of bottled waters (non-carbonated and carbonated)

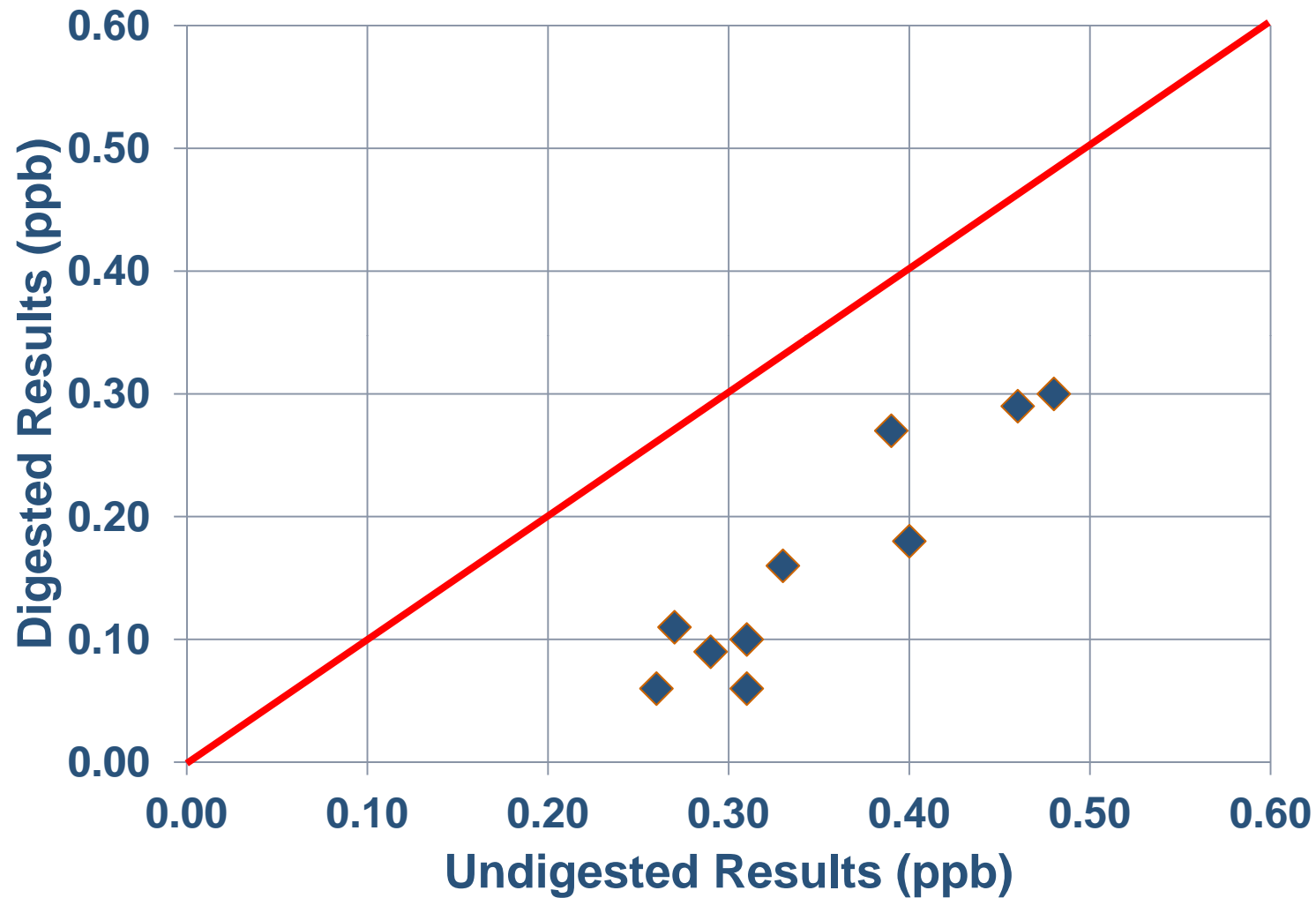
Does Digestion Solve the Carbon Interference Problem?



Another Demonstration of the Need for Digestion at Low Levels for Total Chromium



Comparison Results for Membrane Effluent Samples for Total Chromium

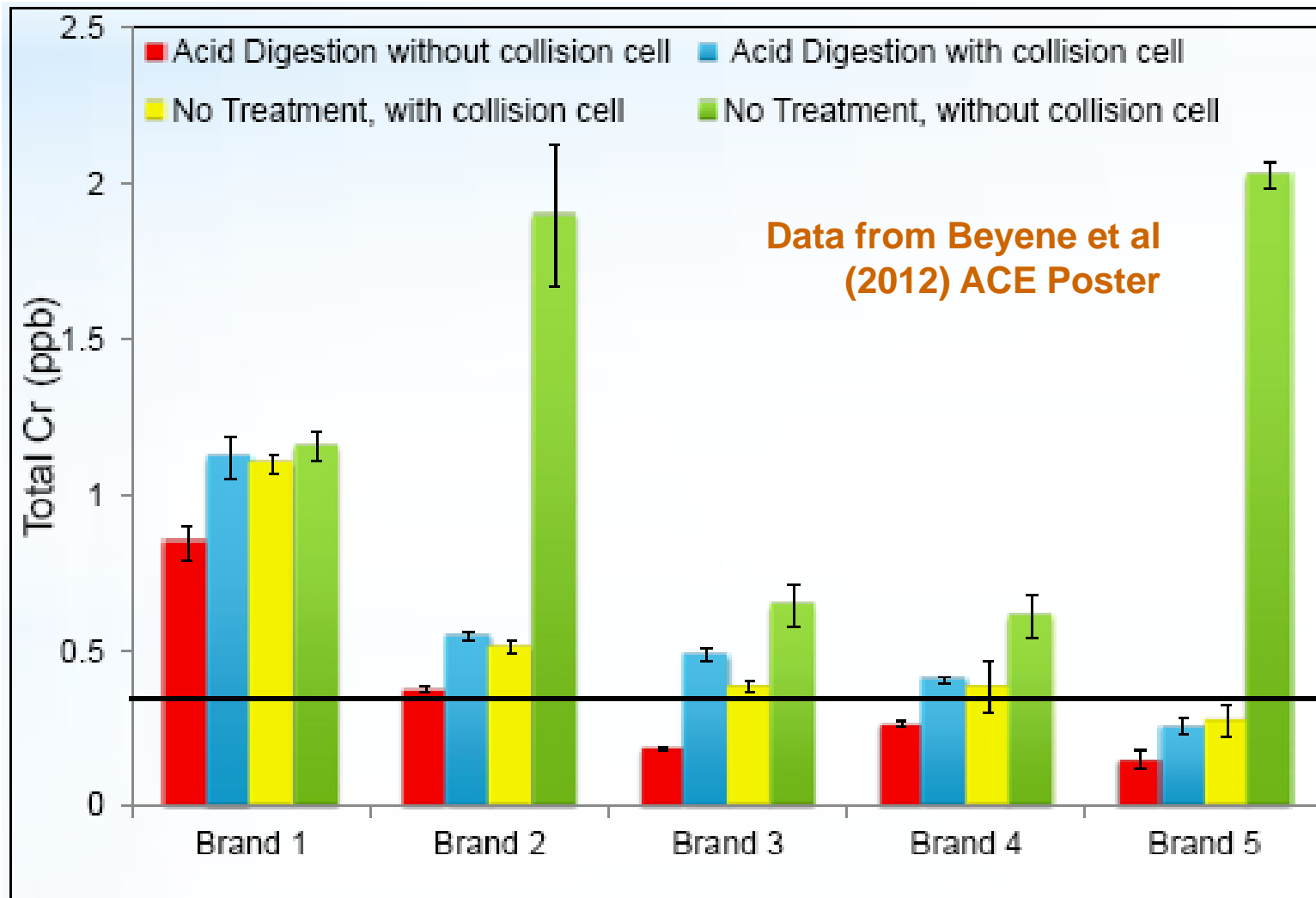


What About Collision Cell As An Option?

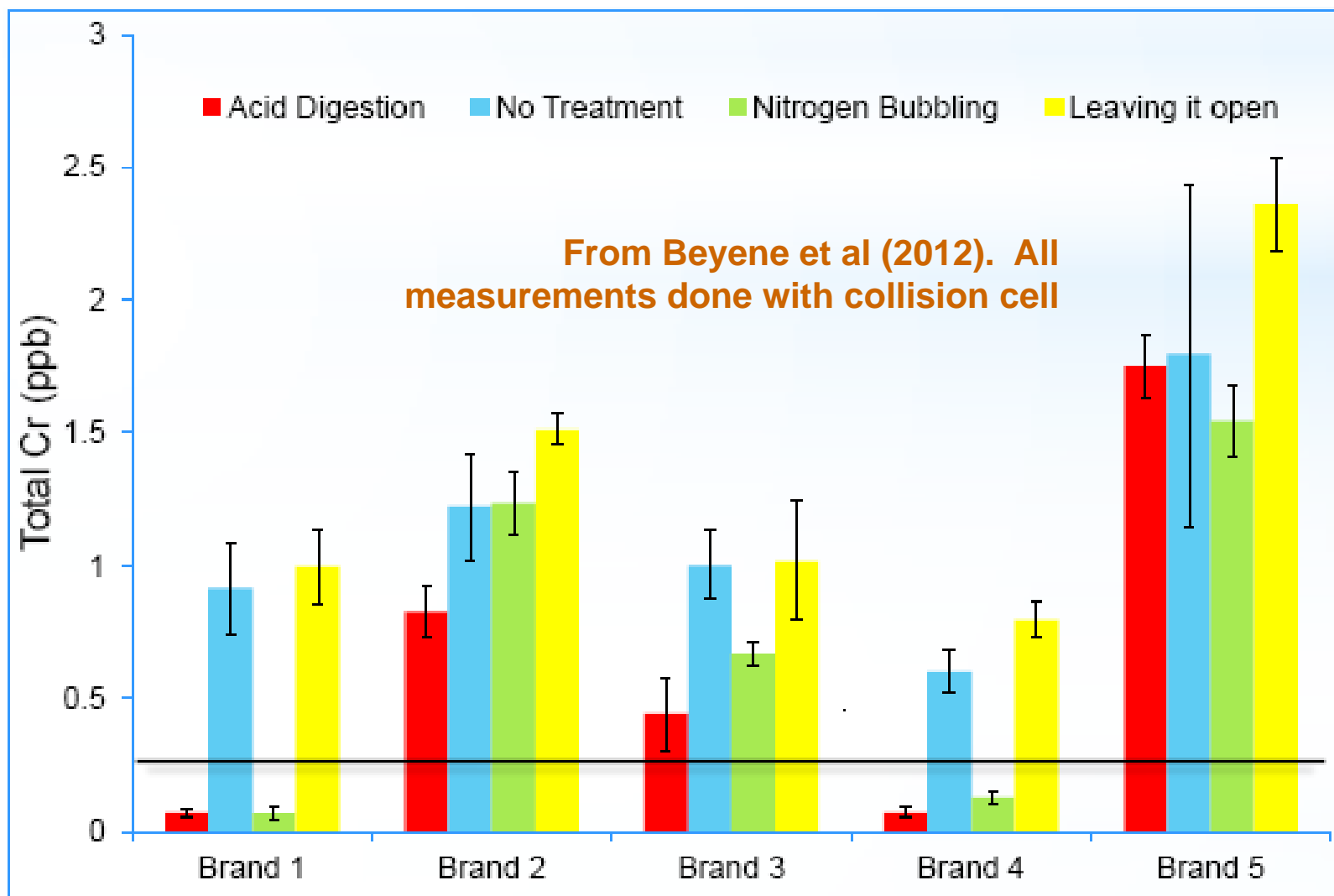


- **Not an approved drinking water method (yet).**
- **Can we evaluate it anyway for accuracy at these low levels?**

Beyene et al (2012) Demonstrated That Prep is Important.



In the Presence of High Carbon (e.g. Carbonated Waters) Digestion or Carbon Removal is Critical



Conclusions- Analytical Methods



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 with nitric acid. Otherwise you may get positive bias (up to low ppb levels).

Collision cell technology may only partially address the bias issues, and is also 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 (VI) is widespread at low levels (ppb to sub ppb). Health effects evaluation and treatment costs will trump occurrence as drivers of regulation. UCMR3 (which will include both Cr (VI) and Cr-T) will provide for a challenging data set for public communications.

Any Questions?



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