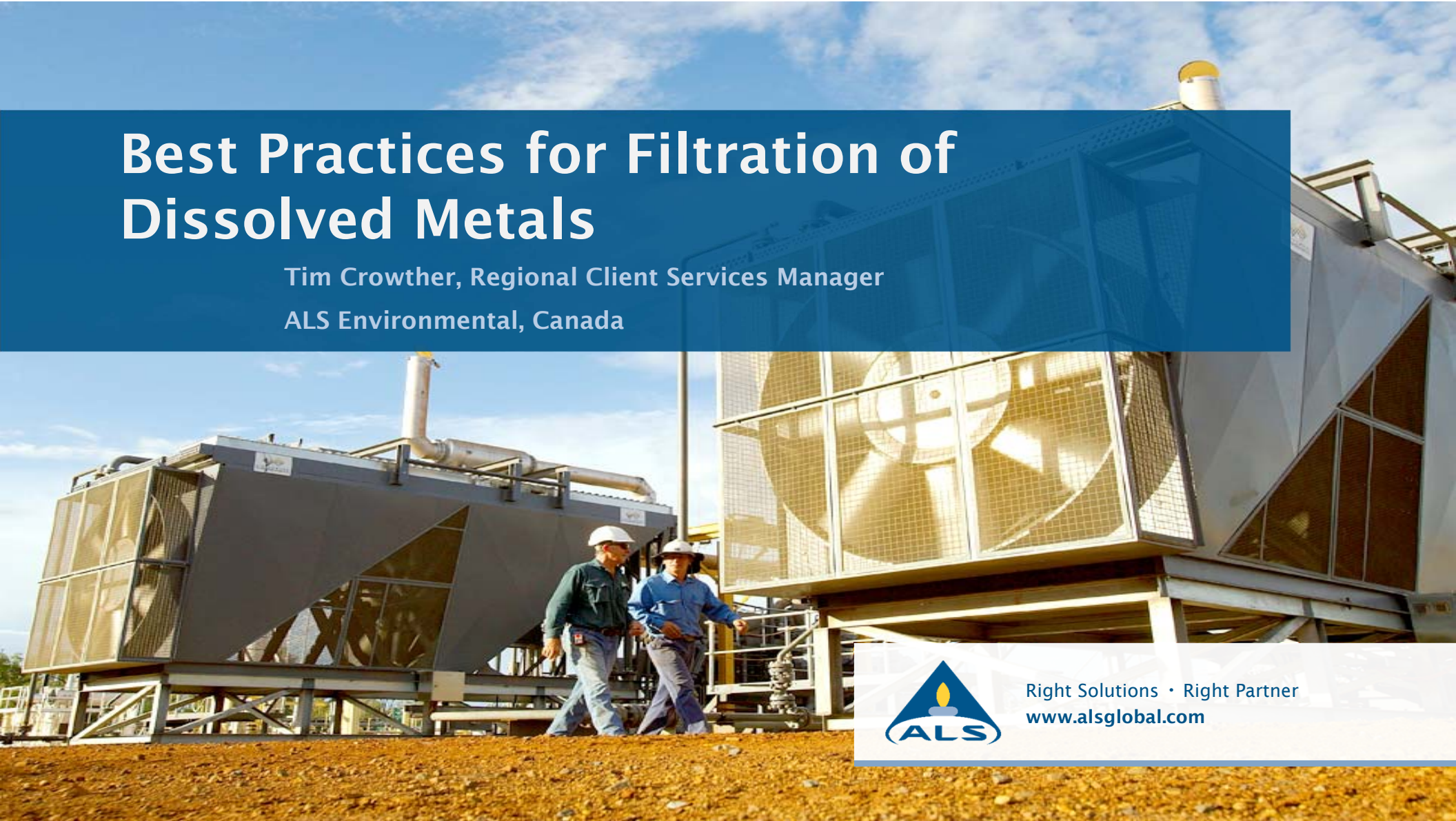


Best Practices for Filtration of Dissolved Metals

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Outline of Presentation



- Why field filtration of dissolved metals is important
- Lab Study 1: Precipitation of Iron & Co-precipitation
 - Comparisons – field vs lab-filtered samples (high iron)
- Lab Study 2: Stability of Unpreserved Mercury
- Field Filtration Techniques – 2 good options
 - In-line Filtration & Syringe Filters
 - Advantages / Disadvantages of each
 - Lab Study 3: In-Line Filter pre-rinsing effects
 - Tips and recommendations for syringe filters
- Preservation Options for Metals & Hg
- Recommended Quality Control

Why Field Filtration of Dissolved Metals is Important



- Dissolved metals behave in complex equilibria!
- Physical & Chemical changes after sampling can drastically change dissolved metals concentrations...
 - Temperature changes
 - Redox changes (e.g. Oxygenation of anoxic samples)
 - pH changes
- Precipitation & Co-precipitation (negative bias)
- Sorption to container or to solids (negative bias)
- Dissolution of particulate matter (positive bias)
- Lab filtered samples can be substantially biased (usually low)
 - Anoxic waters & Mercury are particularly susceptible to biases

Precipitation & Co-Precipitation Effects



- Precipitation of Ferric Oxide/Hydroxide – Common in GW:
 - Ferrous Iron (Fe^{2+}) - quite water soluble; Ferric Iron (Fe^{3+}) - practically insoluble
 - Dissolved Fe^{3+} only exists at <10 ppb in natural waters with pH >5*
 - Dissolved Fe^{2+} can exist at >100 ppm in anoxic waters (groundwaters or deep surface waters)*
 - Fe^{2+} reacts with oxygen; precipitates as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (aka $\text{Fe}(\text{OH})_3$)
 - Orange precipitate, particle size generally > 0.5 μm
 - Oxidation of Fe^{2+} can occur in minutes or a few days (very pH dependent)
 - 2nd order reaction rate w.r.t. hydroxide: +1 pH unit = 100x faster oxidation!
- Precipitation of Iron is widely known, but co-precipitation of other metals is less expected and less understood
- ALS studied co-precipitation of dissolved metals with Fe
 - Compared Field-Filtered vs Lab-Filtered Samples (High Iron)

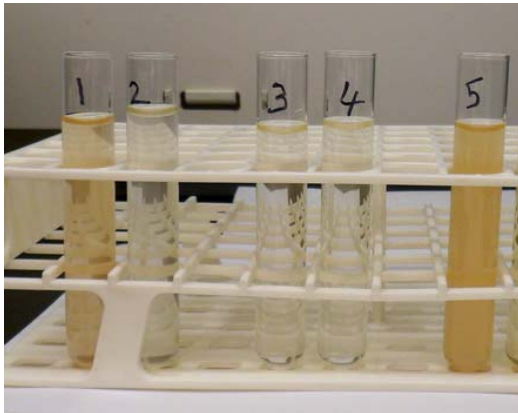
* Chemistry of Iron in Natural Water, US Geological Survey, 1962.

Study 1: Comparison of Lab-Filtered vs Field-Filtered Groundwaters (High Iron)

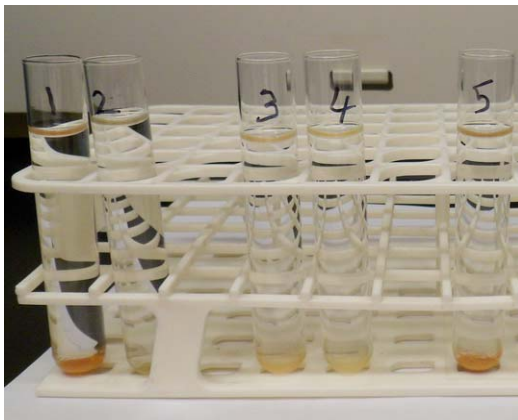


- Identified 5 samples (GW1-5) that met the following criteria:
 - Groundwater (GW) samples
 - Initially field filtered & analyzed for dissolved metals
 - Raw (unpreserved) sample available for study
 - Orange precipitate evident in raw sample
- Raw samples were shaken and lab-filtered (0.45 μ m)
 - Lab filtration occurred 6-10 days after sampling
- Lab-Filtered vs. Field-Filtered results were compared
- Simple but very relevant study
 - Represents actual complex site conditions (worst case?)
 - Only metals present in selected samples could be evaluated

Study 1: Lab Filtration Observations (GW1-5)

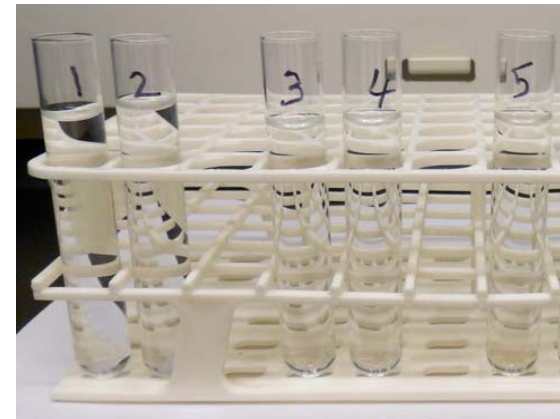


GW1-5: After Shaking



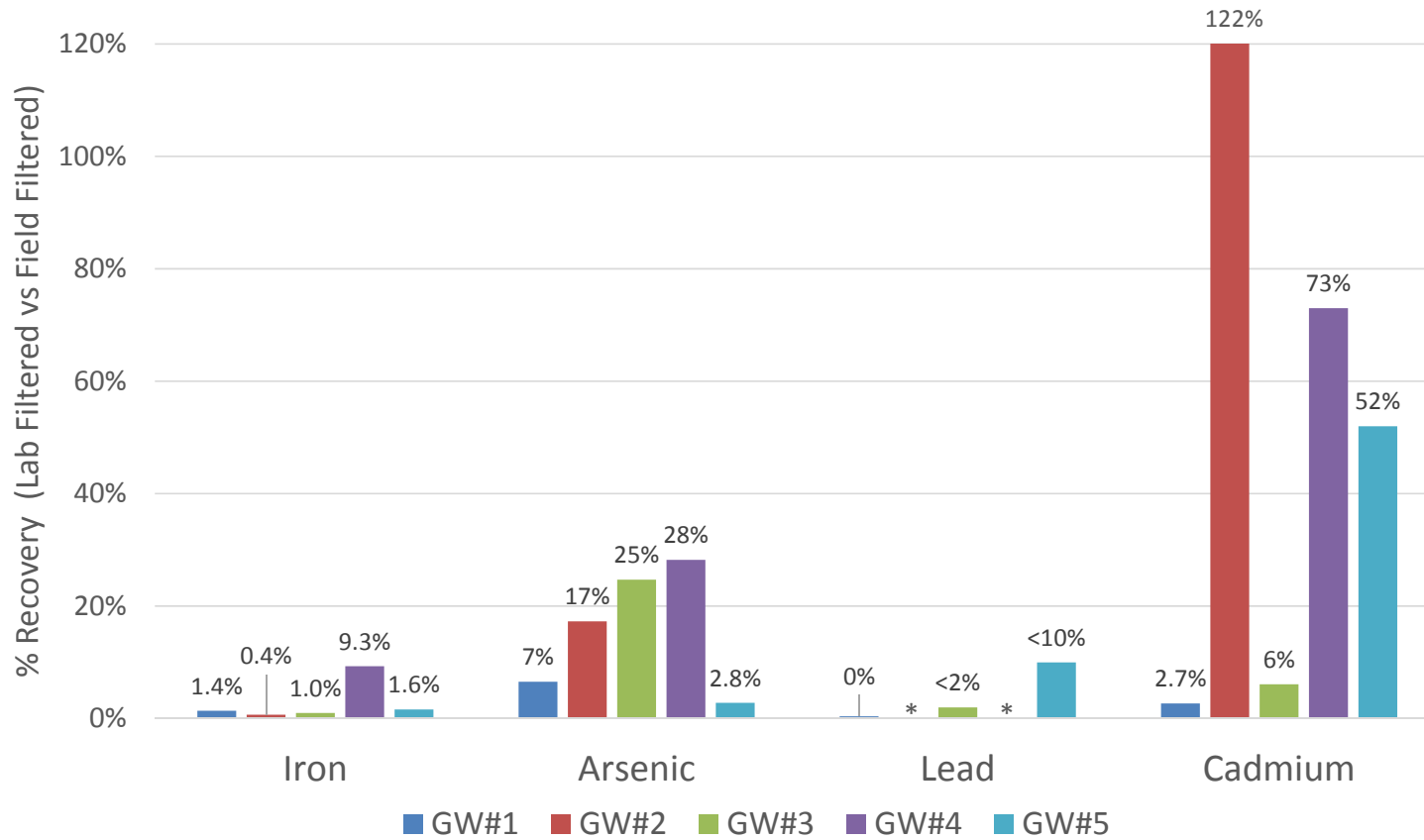
GW1-5: Settled

- All samples showed an orange precipitate, which settles slowly over time
- GW1 & GW5 were highly turbid with highest dissolved iron levels (39 & 63 mg/L)
- Filtered samples were clear
- Precipitate re-dissolves with HNO_3 addition



GW1-5: HNO_3 Acidified (post-study)

Study 1: Lab Filtered vs Field Filtered Metals Results for 5 High-Iron GW Samples (Worst Affected Metals)



* GW#2 and GW#4 were n.d. for Pb

Study 1: Lab Filtered vs Field Filtered Metals Results for 5 High-Iron GW Samples (Worst Affected Metals)



Iron

Sample	Field Filtered (mg/L)	Lab Filtered (mg/L)	Recovery
GW1	39.3	0.547	1.4%
GW2	5.20	0.0231	0.4%
GW3	7.27	0.0742	1.0%
GW4	8.64	0.805	9.3%
GW5	62.5	1.02	1.6%

Lowest 2017 CSR Fe Std = 5 mg/L

Lead

Sample	Field Filtered (ug/L)	Lab Filtered (ug/L)	Recovery
GW1	20.7	<0.05	0%
GW2	nd	nd	
GW3	2.02	<0.05	<2%
GW4	nd	nd	
GW5	0.54	<0.05	<10%

Lowest 2017 CSR Pb Std = 10 ug/L

Arsenic

Sample	Field Filtered (ug/L)	Lab Filtered (ug/L)	Recovery
GW1	19.8	1.30	6.6%
GW2	41.6	7.19	17%
GW3	17.5	4.32	25%
GW4	748	211	28%
GW5	19.6	0.55	2.8%

Lowest 2017 CSR As Std = 10 ug/L

Cadmium

Sample	Field Filtered (ug/L)	Lab Filtered (ug/L)	Recovery
GW1	0.45	0.012	2.7%
GW2	0.127	0.155	122%
GW3	1.02	0.063	6.1%
GW4	1.29	0.938	73%
GW5	0.131	0.068	52%

Lowest 2017 CSR Cd Std = 4 ug/L (for hardness > 210 mg/L)

red = over lowest CSR std
green = under lowest CSR std

Study 1: Lab Filtered vs Field Filtered Metals Results for 5 High-Iron GW Samples (Example Results – All Metals)



Element	Lowest Observed Recovery (%) Lab-Filtered vs Field-Filtered	Example - Sample GW1		
		Field-Filtered Result (mg/L)	Lab-Filtered Result (mg/L)	Recovery (%)
Aluminum	11%	0.0125	0.00134	11%
Antimony	41%	0.00110	0.00054	49%
Arsenic	0.7%	0.198	0.00130	0.7%
Barium	51%	0.0694	0.0434	63%
Cadmium	3%	0.000450	0.0000123	3%
Chromium	<48% (n.d.)	0.00017	<0.00010	<59%
Copper	<18% (n.d.)	0.00063	<0.00020	<32%
Iron	0.4%	39.3	0.547	1.4%
Lead	0.2%	0.0207	<0.000050	0.2%
Molybdenum	38%	0.000854	0.000327	38%
Selenium	<12% (n.d.)	0.00043	<0.000050	<12%
Silver	<13% (n.d.)	0.000076	<0.000010	<13%
Uranium	55%	0.00141	0.000781	55%
Vanadium	<50% (n.d.)	0.0010	<0.00050	<50%
Zinc	25%	0.023	0.0057	25%

Red: test result is above lowest 2017 CSR std

Green: test result decreased from above to below lowest 2017 CSR std



Study 2: Stability of Dissolved Mercury (Hg)

- Mercury in water is preserved with HCl or BrCl
 - Glass or Teflon containers required
 - Literature indicates Chloride is key to stabilization of Hg in water, due to formation of HgCl_4^{2-} (≥ 30 mg/L Cl^- required)*
- How stable is Mercury in unpreserved waters?
- ALS conducted a simple stability study:
 - 3 Hg Spike levels: 10 ppt, 100 ppt, & 1 ppb + Control
 - De-ionized water, neutral pH
 - Glass containers, no preservation
 - Tested concentrations over 28 days

*Louie et al., Anal. Methods, 2012, 4, 522

Study 2: Stability of Unpreserved Dissolved Mercury



Time	Blank	10 ppt	100 ppt	1 ppb	Control 100ppt (w/HCl)
		Recovery	Recovery	Recovery	Recovery
0	<5 ppt	99%	83%	88%	94%
2 hrs	<5 ppt	76%	87%	85%	100%
4 hrs	<5 ppt	60%	81%	85%	91%
24 hrs	<5 ppt	50%	72%	84%	100%
7 days	<5 ppt	20%	55%	76%	109%
14 days	<5 ppt	23%	33%	48%	88%
21 days	<5 ppt	0%	15%	41%	101%
28 days	<5 ppt	0%	10%	30%	97%

Conditions: De-ionized water, no preservative, neutral pH, glass container.

Qualification: Dissolved Mercury stability is complex; each sample may behave differently!

Field Filtration - Two Recommended Options



In-Line Filters



Syringe Filters



Filtration Using In-Line Filters – Pros and Cons



- Best option for filtration of large volumes from groundwater wells
- Convenient & high capacity
 - But requires specialized sampling pumps (and power)
- Filter cost is high: ~\$25 per filter (single use)
- Sampling large GW volumes may cause well disturbance
 - Turbid, disturbed samples not representative of GW can result
 - Disturbed GW samples may cause false positives for some tests
- Cleanliness and background levels?

Study 3: In-Line Filter Pre-Rinse Assessment



- Is pre-rinsing of In-Line Filters necessary?
 - Some filter suppliers suggest no rinsing is needed
 - DL requirements vary dramatically between users
 - What metal concentrations could result from non-rinsed filters?
- ALS conducted an In-Line Filter pre-rinse study (2011)
 - 4 different commercially available filters
 - Tested each filter with no rinsing, & after 1.25L rinsing
 - 250 mL samples collected
 - 2 or 3 replicates per filter
 - Ultra Trace Dissolved Metals tested by High Resolution-ICPMS
 - Results reflect filters from 2011 - likely just as relevant today

Study 3: In-Line Filter Pre-Rinse Study (Summary Data)



PARAMETER	ALS Routine DL (ug/L)	ALS Ultra Trace DL (ug/L)	Lowest 2017 CSR Std (ug/L)	Filter A NO RINSE n=3 (ug/L)	Filter B NO RINSE n=2 (ug/L)	Filter C NO RINSE n=2 (ug/L)	Filter D NO RINSE n=2 (ug/L)	Filter A 1.25 L RINSE n=3 (ug/L)	Filter B 1.25 L RINSE n=2 (ug/L)	Filter C 1.25 L RINSE n=2 (ug/L)	Filter D 1.25 L RINSE n=2 (ug/L)
Barium	0.05	0.02	1000	0.85	0.2	0.031	0.081	0.15	<	<	<
Cadmium	0.005	0.005	0.5	<	0.008	<	<	<	<	<	<
Calcium	50	10	1,000,000	1,000	146	44	19	16	16	<	<
Chromium	0.1	0.1	8	<	<	<	<	<	<	<	<
Copper	0.2	0.05	20	4.6	0.19	1.9	2	0.47	<	0.067	0.15
Lead	0.05	0.005	10	0.033	0.017	0.0072	0.083	0.0065	<	<	0.012
Lithium	1	0.5	8	12	<	<	<	<	<	<	<
Magnesium	5	5	n/a	146	26	<	<	<	<	<	<
Manganese	0.1	0.02	200	0.18	0.068	0.027	0.039	<	<	<	<
Potassium	50	5	n/a	250	22	15	120	6.1	<	<	<
Sodium	50	10	200,000	1,900	37	69	200	55	<	<	<
Strontium	0.2	0.2	2,500	5.5	0.63	<	<	<	<	<	<
Tin	0.1	0.01	2,500	0.053	<	0.016	0.01	<	<	<	<
Zinc	1	0.5	75	12	0.51	2.3	3.6	4.2	<	<	<

Red: exceeds lowest CSR std
 Orange: exceeds ALS routine DL
 Yellow: exceeds 1/2 ALS routine DL
 Blue: exceeds ALS ultra-trace DL

Highest of 2 or 3 replicate results shown



Syringe Filters – Pros and Cons

- Best-suited for filtration of small sample volumes
 - A 60 mL syringe fills a 60 mL metals bottle in one step
- Small sampling volume supports low flow sampling
 - Good for wells with very low recharge rates
 - Pumping less sample leads to less turbid, better quality GW samples
- Simple to use; no special equipment or power needed
 - Best option for surface waters if sampling pumps not used
- Low cost (single-use): ~\$3 per sample w/60 mL syringe
- Lab-proofed syringe filters suitable for trace metals
 - Only use syringe filters supplied or recommended by your lab!
 - Also suitable for many other dissolved analytes (DOC, phosphate, etc.)
- Highly turbid samples can cause filters to plug
 - Less problematic with smaller sample bottles

Tips for Syringe Filtration

- Use syringes & filters provided/recommended by your lab
 - Must be proofed as suitable to meet required DLs
- Preferred procedure:
 - Use clean disposable gloves (change often!)
 - Do not touch any surfaces that will contact sample
 - Remove plunger (hold in one hand)
 - Install filter tightly to syringe with Luer-lock
 - Pour sample into syringe barrel (fill to ~60 mL line)
 - Install plunger
 - Discard first 2 mL of sample to pre-rinse filter
 - Apply pressure and filter sample into collection bottle
 - Replace filter if plugged (for very turbid samples)
- Use a syringe filtration assist device!
 - Especially if filtering many samples, or turbid samples



Syringe Filtration Assist Devices



Plexiglas Syringe Filter Holder

- ALS-recommended practice for syringe filtration
- Reduces manual strain
- Generates higher pressure for filtration of turbid samples
- No metal parts!
- No electrical power required
- ALS can provide these devices at reasonable cost
- Smaller version is planned (miniaturized for 60 mL bottles)

Syringe Filtration Assist Devices



Caulking Guns

- Reduces manual strain
- No electrical power required
- Composite (plastic) construction preferred to minimize metal parts
 - Use caution to prevent contamination from metal parts
 - Replace immediately if any signs of oxidation of metal parts are seen
- Very low cost

Metals and Mercury Preservation Options



- After field filtration, D-metals are preserved with acid:
 - Nitric Acid (HNO_3) preserves metals
 - Hydrochloric Acid (HCl) preserves Mercury (Hg)
- Option 1: Field Preservation
 - Traditionally done by addition of acid vials in the field
 - Field preservation using “pre-charged” sample bottles (provided by the lab) is a convenient and newer option
 - Do not pre-rinse sample bottles if pre-charged!
- Option 2: Lab Preservation
 - Metals & Hg water samples can be lab-preserved within 14 days of sampling (28 days for Hg), in original containers (metals/Hg will re-dissolve)
 - Applicable to T or D (Dissolved samples must be field filtered)
 - Avoids hazards & contamination issues with field use of acids
 - Samples must equilibrate at the lab after preservation (16-24 hr minimum)
 - Recommended practice by US EPA and BC MOE

Recommended Quality Control – Filter Blanks!



- Filter Blanks - Highly recommended as D-Metals Field QC!
 - Labs can provide metal-free deionized water
 - Filter Blanks are easy to prepare with syringe filters or in-line filters
 - Especially important for ultra trace metals testing
 - The only way to know whether low level detections are real!
 - Not commonly used but they should be!!!
- Dissolved > Total Metals Issues are Extremely Common!
 - ALS sees thousands of D>T metals (exceeding by >20%) each year
 - Trace metal contamination during field filtration is very common

Summary & Conclusions



- Field filtration is always the best practice for accurate and defensible testing for dissolved metals
 - For anoxic high iron samples, extreme losses of many heavy metals can occur quickly due to co-precipitation with iron oxide
 - Field filtration is crucial for dissolved metals in groundwaters
 - Field filtration is crucial for dissolved mercury in any waters
- Two recommended options for field filtration:
 - In-Line Filtration
 - Best where filtration of large sample volumes are needed
 - Pre-rinsing is highly recommended (minimum 1 L for routine DLs)
 - Use filters & rinse volume proven suitable for your DL requirements
 - Syringe Filters
 - Most suitable for small sample volumes
 - Very low cost, no special equipment needed
 - Suitable for trace or ultra-trace metals (using lab-proofed filters)
 - Syringe filtration assist devices simplify use!
- Metals & Hg preservation can be done in the field or at the lab
- Field Filter Blanks are highly recommended as QC!



Thanks for your attention...