



EnviroMail 06

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Best Practices to Prevent False Positives & Negatives for Dissolved Metals

British Columbia Regulatory Update

Further to the earlier content published below, due to broader recent awareness that delayed filtration can cause severe negative bias of dissolved metals, BC ENV (the BC Ministry of Environment & Climate Change Strategy) has issued a requirement, effective May 1, 2020, for field filtration of all water samples that will be tested for dissolved metals (including mercury). The new requirement applies to all regulatory compliance monitoring under the BC Environmental Management Act, which includes the BC Contaminated Sites Regulation, Hazardous Waste Regulation, and environmental discharge permits under provincial authority. After May 1, the ALS Vancouver laboratory will add report qualifiers for any dissolved metals samples that are not field-filtered. All ALS Canada laboratory test reports already indicate the location of filtration (field or lab) for all dissolved metals tests.

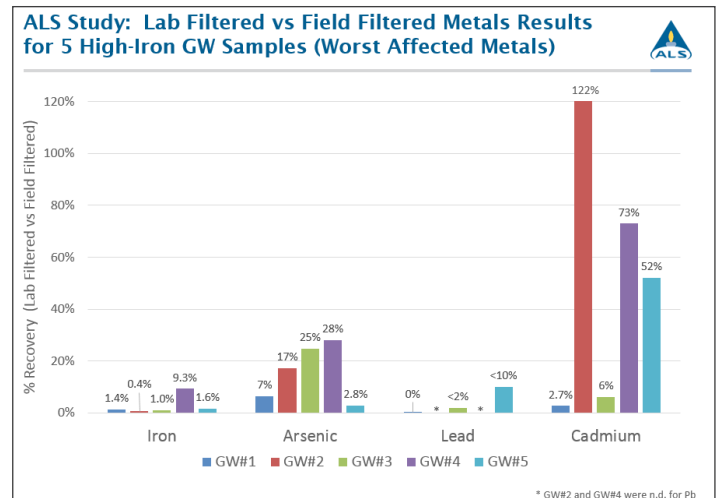
Field Filtration as Best Practice

Most environmental practitioners understand that field filtration is considered the best practice when collecting water samples for dissolved metals testing, but many people may be unaware of the causes and potential magnitude of negative consequences associated with delayed filtration. Dissolved metals in water exist in complex equilibria, which can be impacted by many physical and chemical factors, particularly changes to redox conditions, pH, or temperature, which can trigger changes to dissolved metals concentrations due to precipitation, co-precipitation, sorption, or dissolution of particulate matter. These factors can cause significant positive or negative bias to dissolved metal concentrations, sometimes to an extreme degree. The only way to ensure that water samples collected for dissolved metals will accurately represent conditions at the time of sampling is to conduct filtration in the field, preferably immediately after sample collection.

Co-Precipitation of Dissolved Metals with Iron

Perhaps the most common pitfall resulting from delayed filtration of dissolved metals is caused by the precipitation of iron oxides and

associated co-precipitation of other metals. This happens because Ferrous Iron (Fe²⁺) is relatively water soluble (up to > 100 mg/L), whereas Ferric Iron (Fe³⁺) is practically insoluble in water under normal environmental conditions (generally < 10 µg/L). Ferrous Iron exists and is stable in anoxic waters (e.g. many groundwaters), but when an anoxic water sample is exposed to air, oxidation of Ferrous Iron to Ferric Iron can occur rapidly, sometimes in as little as five or ten minutes (oxidation rate increases substantially with higher pH). When iron precipitation



occurs in a sample, other metals can co-precipitate, causing substantial changes to the overall dissolved metal composition of the sample. This is a well-known phenomenon, and precipitation of iron under these circumstances is expected, but co-precipitation of other metals is generally less understood.

ALS Co-Precipitation Impact Study

ALS recently studied the impact of iron precipitation on the co-precipitation of other metals with a series of high-iron groundwater samples, and found substantial losses of most dissolved metals (in comparison to field filtered metal concentrations), with losses up to 100% in several cases

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where filtration was delayed (by 6 to 10 days in these somewhat worst-case examples). Arsenic, Lead, and Cadmium were particularly impacted by co-precipitation, in addition to the expected loss of Iron, but most dissolved metals were impacted to some degree. A summary of the ALS study results for Arsenic, Lead, Cadmium, and Iron are shown in the chart above.

For these 5 samples, Arsenic losses averaged over 80%, lead losses averaged over 95%, and Cadmium losses varied significantly by sample, ranging from zero to 97% loss. The impact on sample results can clearly be seen, with many of the test samples potentially having key metal concentrations underestimated by a factor of 10 to 100 times if correct field filtration techniques were not employed. This study also highlights the necessity of field filtration for the analysis of dissolved ferrous iron.

Recommended Field Filtration Techniques

ALS recommends the use of syringe filtration for convenient filtration of dissolved metals samples in the field, using disposable syringes and syringe filters that have been proofed for suitability and/or recommended by the lab. Low cost syringe filters and syringes are available that are suitable for ultra-trace level metals analysis (approximately \$3 CAD per sample, far less than the cost of in-line filters).

Using a 60 mL disposable syringe and syringe filter is very convenient, especially when used with smaller 60 mL sample bottles, which minimizes the amount of sample to be filtered, and also reduces the likelihood of having to use multiple filters for highly turbid samples. In addition, in the event that a sample matrix proves challenging to filter (e.g. a groundwater with suspended clay), ALS can perform the required analysis on a 60 mL bottle which is only half full, however the lab may only be able to perform the initial analysis plus one duplicate analysis so this is not preferred.

ALS also recommends the use of a specially designed Plexiglas syringe filter housing device (shown at right, available from ALS Canada labs). The use of this device simplifies the filtration process, reduces manual strain, and is convenient because it requires no electrical power and has no metal parts that could contribute to contamination of samples.

Some caulking guns are also suitable to assist with syringe filtration, however caution is required for their use, since most caulking guns do contain metal parts. If in-line filters are used, ALS recommends pre-rinsing of the filters with 1L of sample to rinse out most residual

contaminants from the filter (or using an alternate volume proven to be suitable for your filter type).

Field Filtration Blanks are Highly Recommended!

ALS highly recommends the collection of Filtration Blanks whenever field filtration is conducted, as a control of metals background levels that may be contributed by the filtration process. This is the only way to monitor and control against contamination, which is a common problem with many types of filtration media. The lab can provide de-ionized water to facilitate the collection of Filtration Blanks.

Field Filter to Avoid False Positives and False Negatives!

Using best-practice field filtration techniques, it is relatively straightforward to collect high quality water samples for dissolved metals, without significant risk of contamination, and avoiding the danger of sample changes over time due to precipitation or co-precipitation.



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