## SECTION C.5

Gel Sampler

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Trace metal biological availability is poorly represented by conventional water sampling approaches. It is now well known that metal toxicity is strongly influenced by complexation reactions that occur in all natural aquatic systems. Thus, in many instances, trace metal availability to aquatic organisms is significantly different from either the total or dissolved metal concentration.

The recently developed gel-sampler accumulates biologically-available metals (*i.e.*, that fraction that is both dissolved and uncomplexed) onto an ion-specific resin. Particulate and strongly complexed metals are excluded in the same way that they are unavailable to biota. The behaviour of the sampler has been "calibrated" in the field and laboratory and has demonstrated a strong correlation to biological-availability as determined through bioassays on several test organisms.

The sampler is very easy to use and deploy, and obviates many of the classic problems encountered by conventional water sampling technologies. Advantages of the gelsampler include:

- Direct measurement of trace metal biological availability;
- Preservation and direct determination of metal speciation;
- Elimination of the need for sample filtration;
- Elimination of contamination during sample collection;
- Elimination of the need to ship water samples;
- Ability to easily archive samples for comparatively long periods of time;
- Preconcentration of metals thereby improving detection limits;
- Removal of metals from the sample matrix for improved analysis;
- Integration of biologically-available metal concentration with time;
- Insensitivity to changes in salinity from fresh water through seawater.

In order to test the performance of the gel-sampler, chronic and acute bioassays were conducted on a suite of test organisms. This note summarizes one of the acute lethality tests for copper on rainbow trout.

The rainbow trout 96-hour  $LC_{50}$  bioassay is an industry-standard test. In this case, rainbow trout were exposed to "dissolved" copper concentrations ranging from 2 to 500  $\mu$ g/L (Figure 1). Two parallel tests were run: 1) trout exposed to five different concentrations of dissolved copper; and 2) trout exposed to five different concentrations of dissolved copper in the presence of excess <sup>1</sup>EDTA.

<sup>&</sup>lt;sup>1</sup> EDTA is a strong organic complexing agent (i.e., it binds copper strongly) and was added in excess to each treatment such that the majority of the dissolved copper was complexed. Copper complexed by EDTA passes through filter membranes and is therefore part of the "dissolved" fraction as determined by conventional sampling approaches.

The sampler units were deployed during the bioassay for a period of approximately 12 hours. The data are summarized in Figure 1 which presents the concentration of "dissolved" copper (as measured by ICP-MS) on the x-axis (both with and without EDTA); the corresponding labile or bio-available concentrations as measured by the Gel-Sampler are presented on the y-axis.

In the bioassays which included EDTA, all organisms survived regardless of the dissolved concentration; however, in the "organic-free" case, mortality observed at dissolved concentrations of >50 μg/L. As anticipated, "dissolved" copper concentration presented a very poor representation of toxicity when dissolved organic matter was present in the test; the "dissolved"

copper concentrations were identical both with and without EDTA.

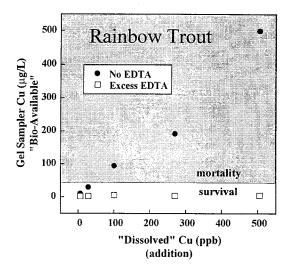


Figure 1 – Bio-available Cu (as measured by the gelsampler) vs. "dissolved" Cu (added as a metal spike) with and without the complexing agent EDTA. The shaded zone indicates the concentrations in which trout mortality was observed.

However, the gel sampler showed markedly lower bio-available copper in the EDTA-complexed bioassay, which corresponded to higher survival. The differences between the two cases indicate that the gel sampler yields a much-improved reflection of bio-availability over conventional sampling approaches.