February 3, 2017

To: Jason Pappani, Water Quality Standards Coordinator, IDEQ
From: Chris Mebane, Water Quality Specialist, USGS

Subject: Comments on Idaho's Draft Implementation Guidance for the Idaho Copper Criteria for Aquatic Life

Thank you for the opportunity to review your 20 December 2016 draft guidance for implementing the proposed biotic ligand model (BLM)-based aquatic life criteria for copper. The document reflects the careful thought that your team has given the problem. I have some comments and suggestions which are focused on data representativeness and quality considerations with pH and dissolved organic carbon (DOC). As noted, the BLM is most sensitive to DOC and pH, both of which vary over space and time. Further, DOC samples are easily contaminated during sample collection and processing. The nature of the variation in pH and DOC contamination issues would likely skew criteria values towards being underprotective, and some cautions in the document might be prudent. The document does a good job describing seasonal differences in DOC. It might be helpful to re-arrange the discussion by adding a new sub-section around 4.3 "*Considerations on variation in BLM parameters over time*" or something like that.

Daily cycles in pH

In some streams, daily cycles in pH could have important implications to BLM-based criteria. In the example below, pH cycled from about 7.5 to 8.5 daily. Calculating the BLM-based Cu criteria assuming parameters other than pH and temperature were constant results in chronic Cu criterion (CCC) values cycling between about 8 to 25 µg/L. The minimum Cu criterion concentrations occurred between about 04:00 to 08:00 am and the maximum values occurred between about 4 to 6 pm. If receiving waters for a discharge had similar characteristics, whether the criterion value was calculated at 8 or 25 µg/L could be important. Even a 0.5 unit pH change, such as that occurring between about 08:00 and 11:00 am in this example, would result in nearly doubling the CCC from about 8 to 15 µg/L (Figure 1). The issue of daily cycling in streams can be important for metals toxicity, or the lack thereof. Working in mining-affected streams in Montana, Balistrieri and others [1] found that only slight differences over a critical range in water composition, which determines the speciation of biotic ligands, can have a large effect on fish survival, ranging from 10% to 90% mortality. In addition to being environmentally important, a 2-3 fold difference in criteria values depending only on the time of day sampled would likely be important to interested dischargers.

This begs the question – in waters with pronounced daily pH cycles, what is the most appropriate approach to use for criteria calculation? The lowest "critical" pH? The average? Any haphazard value obtained from whenever the sample happened to be measured? Direct evidence on this point appears to be sparse. Caged cutthroat trout in streams exposed to daily cycles in metals concentrations and pH, and with time-intensive monitoring, were compared to other trout were exposed to constant concentrations that were similar to the average concentrations from the caged trout [1,2]. BLM modeling suggested that observed mortalities better matched the time-integrated concentrations than did the peak mortality conditions predicted from the most severe daily conditions [1]. It is also important to keep in mind that notions of "critical" pH conditions will flip with different metals or contaminants. With Cu and Pb,

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lower pHs are expected to be associated with higher bioavailability and toxicity, but with metals such as Cd, Ni, and Zn and ammonia, higher pH is expected to result in increased toxicity.
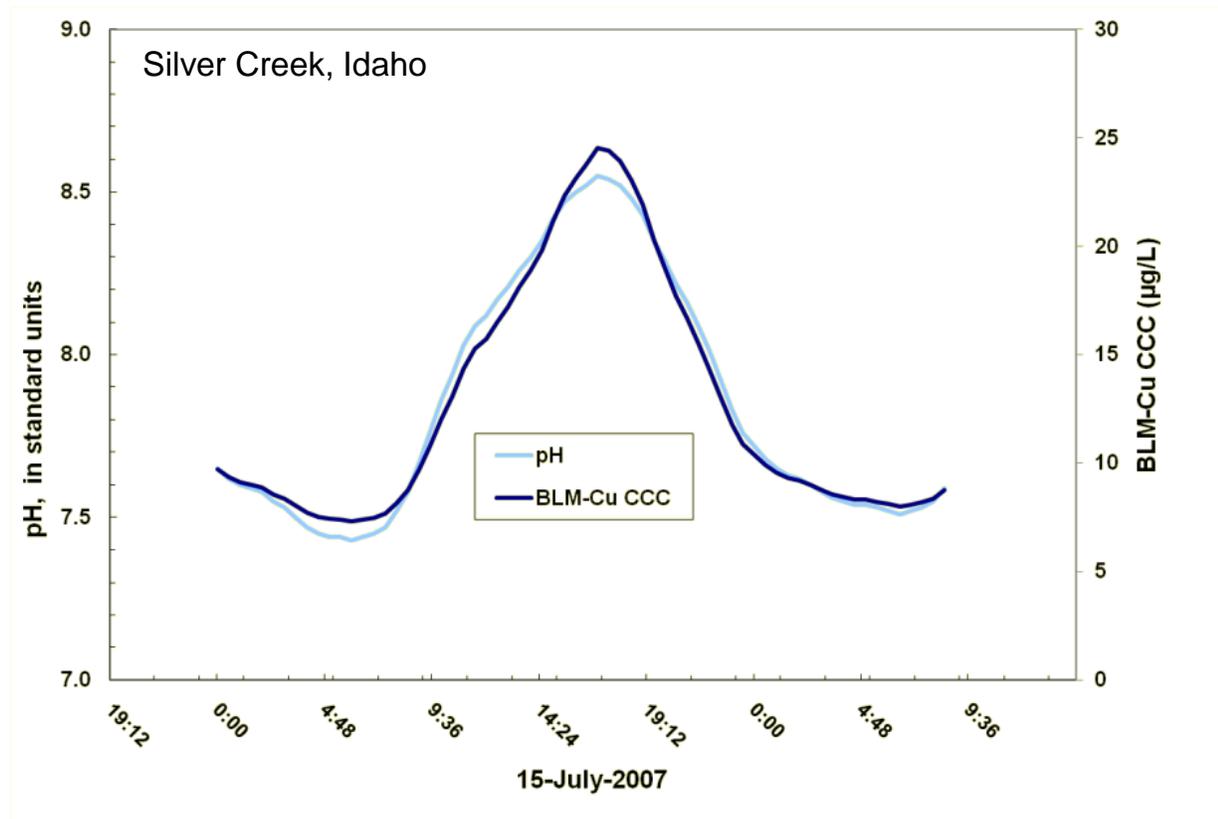

Figure 1. Figure 1. Example of the potential influence of daily pH swings on BLM-based Cu criteria, calculated assuming major ions and DOC are constant, varying pH and temperature

I would suggest the most appropriate guidance may be to strive match the averaging period for pH measurements with the averaging period of the criterion. Thus, in principle, a 1-hour average pH would apply to the acute criterion calculation, and a 4-day average pH would apply to the chronic. In practice, no one is likely to collect multiple BLM parameters over an hour, and rather a single pH measurement would be matched with discrete samples for acute criteria comparisons. As pH swings in a given waterbody are typically similar day to day (assuming stable weather and flows), a 4-day record probably doesn't give a lot more information than would a single daily pH cycle. Further, as the daily timing of pH troughs and peaks are predictable, discrete measurements at about 08:00 am and 4 pm would likely catch most of the range, and the midpoint of the range would be close to the average.

The example given with a 1-unit range, is greater than expected for some receiving waters, although a 2-unit swing was measured in Silver Bow Creek, Montana, a largely open canopy stream that receives urban effluent [1]. I haven't done any systematic reviews, but from monitoring I've done or followed in Idaho streams, I suspect a daily swing on the order of 0.5 units might be typical for small to mid-order streams, although small mountain streams can have daily cycles of only 0.1 units or so. While

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generalizations on productivity of streams (which drives pH swings) by size and form could be made, for dischargers, obtaining actual measurements of daily pH cycles should be encouraged. These are not difficult to obtain and would be more reliable than assumed adjustments based on potential ranges and measurement time of day.

The problem of DOC sample contamination

DOC is an obnoxious parameter to work with because it isn't stable in water samples and sample filtration and bottles can be a major sources of contamination. This issue has been well known in the oceanographic community [3,4], but environmental monitoring practitioners seem largely unaware of the issue. For instance, both Standard Method 5310B for determination of total organic carbon in water and the corresponding EPA method 415.3 simply say that the DOC procedure is the same as for TOC, but that the sample needs to be passed through a 0.45-μm filter prior to analysis to remove particulate organic from the sample.

The issue that the 0.45 µm filtration approach commonly used for trace metals may be inappropriate for DOC is a non-trivial matter. Norrman [3] reported that up to 24.5 mg/L DOC was recovered from purified Milli-Q water in the first 7.5 mL flush through a 0.45 µm prepackaged syringe filter, and even after 5 rinses, 0.6 mg/L DOC was present in the rinse water. Unfiltered "pure" grade Milli-Q water is currently certified to be less than 0.03 mg/L TOC [this is a mid-grade purified water, also called Type 2 water]. In QA testing by the USGS National Water Quality Laboratory, 0.45 µm capsule filters that were certified for trace metal sampling were found to introduce high DOC contamination, up to 21 mg/L in the first flush, and even after a full liter flush of organic blank water, still introduced measureable DOC (appended). The standard method for collecting DOC in the research community is to use precombusted glass fiber filters in a polycarbonate housing [3-5], but this method might be too much hassle for routine discharge monitoring without practice.

Storage of DOC samples prior to analysis is another source of uncertainty, as degradation (losses) can occur with stored samples. Table 1 in the draft guidance appears to be mostly follow 40 CFR, Ch.I, Part 136.3, *Identification of Test Procedures for non-potable water samples* (May 18, 2012), which in turn follows Table 17.1 in EPA's Handbook for Sampling and Sample Preservation of Water and Wastewater [6]. (The exception is Table 1's 7-day hold time vs. 28 days in the EPA references). EPA's Handbook is over 30 years old and appears to represent the best professional judgment of its authors. No evidence or even explanation are given in support of its recommended holding times, and filtration wasn't even mentioned. Acidification is regarded as an ineffective preservation technique in the oceanographic community [7]. Instead, if samples can't be promptly analyzed within a few days, freezing has been recommended in protocols from marine chemistry labs at the University of Washington and University of Miami.

So what to do? A simple scheme would be to take a performance-based blank correction approach in lieu of attempting to prescribe methods that would be effective for all settings. In this approach, each sampling event would include a procedural blank, in which organic blank water or purified water is filtered, preserved, and analyzed in the same manner as the environmental samples. The results of the blank are then subtracted from the environmental samples.

A second suggestion is to add a brief mention of the sample contamination problem in the text near Table 1, with some brief advice on filtering order and flushing for those using capsule filters.

Considering the near ubiquitous use of high capacity capsule filters in projects involving collection of trace metals, and their cost (~$15-30 each) it is likely that some facilities or sampling groups would prefer to simply extend the use of the same filter to DOC samples. In that case, the order of sample collection for filtering BLM parameters through the same capsule filter should be: (1) Trace elements and major cations; (2) Nutrients (if collected); (3) Major anions and alkalinity; and (4) DOC last. Just to collection of DOC, the filter should be additionally rinsed, with at least 1-L of site water. At this stage, the USGS recommends both a 1-L rinse with organic blank water and ambient water [5]. However, the USGS protocols do not reference any studies or present data in support of the protocols, and thus it is unclear whether the extra rinse with organic blank water would provide measureable benefit, considering the multiple previous filtrations and rinses.

Please advise if I can provide further information on these comments, if you would like copies of the references, or if you would like specific language suggestions on the guidance. These review comments were prepared in cooperation with the National Marine Fisheries Service. Mention of trade names is for descriptive purposes and doesn't constituent an endorsement.

References

1. Balistrieri LS, Nimick DA, Mebane CA. 2012. Assessing time-integrated dissolved concentrations and predicting toxicity of metals during diel cycling in streams. *Sci Total Environ* 425:155–168.
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3. Norrman B. 1993. Filtration of water samples for DOC studies. *Marine Chemistry* 41:239-242.
4. Yoro SC, Panagiotopoulos C, Sempéré R. 1999. Dissolved organic carbon contamination induced by filters and storage bottles. *Water Res* 33:1956-1959.
5. U.S. Geological Survey. 2002. Procedures for Processing Samples for Carbon Analysis (5.2.2.C). *in* Wilde FD, ed, *National field manual for the collection of water-quality data*. U.S. Geological Survey. pp 6174
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7. Sugimura Y, Suzuki Y. 1988. A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample. *Marine Chemistry* 24:105-131.

August 6, 2008

Office of Water Quality Water-Quality Information Note 2008.13

Subject: Field Methods—Discontinue use of ▮Brand A▮ **capsule filters for dissolved organic carbon (DOC)**

▮Brand A's particular model of capsule filters (name redacted)▮ beginning with lot number T873, are no longer to be used for filtering samples for analysis of dissolved organic carbon (DOC). Quality-assurance tests run by the Quality-Assurance Section at the National Water Quality Laboratory (NWQL) showed DOC levels between the long-term method detection level (LT-MDL) and the laboratory reporting level (LRL) after a 1-liter rinse. Levels of 18.2 and 21.1 mg/L of DOC were seen in the first 125 mL of the rinse water. Because DOC levels appear to be increasing in recent capsule filter lots, the decision has been made to discontinue the practice of using capsule filters for processing DOC samples.

In lieu of the ▮Brand A▮ capsule filters, the ▮Brand B filters (name redacted)▮ or the 25-mm baked, glass-fiber filter (Q441FLD) can be used for processing DOC samples. The 25-mm filter must be used with the Teflon DOC-25 filter unit (Q444FLD) or a filter funnel and flask (see National Field Manual (NFM) Ch. 5.2.2.C for equipment information and instructions [http://water.usgs.gov/owq/FieldManual/chapter5/pdf/chap5.pdf]. This Note modifies this section of the NFM.